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(19) (CA) **CANADIAN PATENT** (12)

(54) Catalyst and Process for Production of Hydrocarbon

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ABSTRACT OF THE DISCLOSURE

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A process for converting synthesis gas composed of hydrogen and carbon monoxide to hydrocarbons and a catalyst for the same. The process includes the step of contacting at reaction conditions a synthesis gas feed to a catalyst which includes cobalt in catalytically active amounts up to about 60 wt% of the catalyst and rhenium in catalytically active amounts of about 0.5 to 50 wt% of the cobalt content of the catalyst supported on alumina. An alkali metal promoter and further a metal oxide promoter may be added.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process and a catalyst for converting synthesis gas to hydrocarbons, and more particularly to a process using a catalyst comprising cobalt and rhenium on an alumina support and the catalyst as such.

Description of the Prior Art

The reaction to convert carbon monoxide and hydrogen mixtures (defined herein as synthesis gas or syngas) to higher hydrocarbons over metallic catalysts has been known since the turn of the century. This reaction is commonly referred to as the Fischer-Tropsch or F-T synthesis. During World War II, Germany exploited a process employing the F-T synthesis for the production of gasoline and other hydrocarbon products. By 1944 a total of nine F-T plants were operating in Germany. The German process used primarily a catalyst composed of cobalt, magnesium oxide, thorium oxide and kieselguhr, in the relative proportions of 100:5:8:200. Later, most of the thoria was replaced by magnesia, primarily for economic reasons. Currently, commercial Fischer-Tropsch plants are operating in South Africa. These plants use a process employing a precipitated iron-based catalyst which contains various promoters to improve the stability and product distribution.

The common F-T catalysts are nickel, cobalt and iron. Nickel was probably the first substance to be recognized as capable of catalyzing the reaction of syngas to hydrocarbons, producing mainly methane (see, for example, "The Fischer-Tropsch Synthesis" by R.B. Anderson, Academic Press (1984), p.2). Iron and cobalt are able to produce longer chain length hydrocarbons and are thus preferred as catalysts for the production of liquid hydrocarbons. However, other metals are also capable of catalyzing the F-T synthesis. Ruthenium is a very active catalyst for the formation of hydrocarbons from syngas. Its activity at low temperatures is higher than that of iron, cobalt or nickel; and it produces a high proportion of heavy hydrocarbons. At high pressures, it produces a high proportion of high molecular weight wax. Osmium has been found to be moderately active, while platinum, palladium and iridium exhibit low activities (see Pichler, "Advances in Catalysis", vol. IV, Academic Press, N.Y., 1952). Other metals which are active, such as rhodium, yield high percentages of oxygenated materials (Ichikawa, Chemtech, 6, 74 (1982)). Other metals that have been investigated include rhenium, molybdenum and chromium, but these exhibit very low activities with most of the product being methane.

Various combinations of metals can also be used for synthesis. Doping cobalt catalysts with nickel causes an increase in methane production during F-T synthesis (see "Catalysis", vol. IV, Reinhold Publishing Co., (1956), p.29). In U.S. Patent 4,088,671 to T.P. Kobylinski, entitled "Conversion of Synthesis Gas Using a Cobalt-Ruthenium Catalyst", the addition of small amounts of ruthenium to cobalt is shown to result in an active F-T synthesis catalyst with a low selectivity to methane. Thus, these references teach that the combination of two or more metals can result in an active F-T catalyst. In general, the catalysts of these teachings have activities and selectivities which are within the ranges of the individual components.

Combinations of metals with certain oxide supports have also been reported to result in an improved hydrocarbon yield during F-T synthesis, probably due to an increase in the surface area of the active metal. The use of titania to support cobalt or cobalt-thoria is taught in U.S. Patent 4,595,703, entitled "Hydrocarbons from Synthesis Gas". In this case the support serves to increase the activity of the metal(s) toward hydrocarbon formation. In fact, titania belongs to a class of metal oxides known to exhibit strong metal-support interactions and, as such, has been reported to give improved F-T activity for a number of metals (see, for example, S.J. Tauster et al., Science, <u>211</u>, 1121 (1981)). Combinations of titania and two or more metals have also been shown to yield improved F-T activity. In U.S. Patent 4,568,663, entitled "Cobalt Catalysts in the Conversion of Methanol to Hydrocarbons and for Fischer-Tropsch Synthesis", combinations of cobalt, rhenium and thoria and cobalt and rhenium supported on titania are claimed useful for the production of hydrocarbons from methanol or synthesis gas. This patent also indicates that similar improvements in activity can be obtained when cobalt-rhenium or cobalt-rhenium-thoria is compounded with other inorganic oxides. However, titania is the only support specifically discussed. The typical improvement in activity gained by promotion of cobalt metal supported on titania with rhenium is less than a factor of 2. We have found that the addition of rhenium to cobalt metal supported on a number of other common supports results in similar improvements in activity.

The only other examples in the literature of catalysts involving mixtures of cobalt and rhenium refer to completely different chemical reactions. For example, in the Soviet Union Patent 610,558, published June 15, 1978, a catalyst composed of cobalt and rhenium supported on alumina is taught to result in improved performance for the steam reforming of hydrocarbons. Steam reforming of hydrocarbons is a process completely different from hydrocarbon production via F-T synthesis and is believed to proceed by a completely different mechanism. Although some steam reforming catalysts can convert synthesis gas to hydrocarbons, such catalysts are not selective for the production of high carbon-number hydrocarbons (C_3 and above) during conversion of synthesis gas. In fact, most commonly used steam reforming catalysts contain nickel as their active metal, and nickel produces mostly methane when used for syngas conversion.

SUMMARY OF THE INVENTION

It has been found in accordance with the present invention that synthesis gas comprising hydrogen and carbon monoxide can be converted to liquid hydrocarbons by using catalyst and a process employing a catalyst consisting of cobalt and rhenium supported on alumina and promoted with an alkali. As used herein, alkali refers to one or more of the elements lithium, sodium, potassium, rubidium, and cesium of group IA of the periodic table. The catalyst preferably contains from about 5 to 60% cobalt, has a rhenium content between 0.5 and 50% of the amount of cobalt, and an alkali content between 0.5 and 5 atom % of the amount of cobalt. The alumina preferably is gamma alumina.

It has been found that the addition of small amounts of rhenium to catalysts consisting predominantly of cobalt supported on alumina unexpectedly results in greatly enhanced activity of this catalyst for hydrocarbon production from syngas. This is surprising in light of the fact that rhenium supported on alumina shows very low activity, with most of the product being methane. Furthermore, rhenium addition to cobalt supported on supports other than alumina results in catalysts with much lower activity levels. In addition, the more active cobalt plus rhenium catalyst maintains the high selectivity to higher hydrocarbons and the low selectivity to methane found with an alumina-supported cobalt catalyst. It has also been found that the addition of small amounts of an alkali to these catalysts serves to increase the average carbon number of the products produced during F-T synthesis. Both the high activity and the low methane production of cobalt-rhenium on alumina are unexpected in light of the facts that (1) rhenium shows very low activity for F-T synthesis, (2) the main products from F-T synthesis over a rhenium catalyst are methane and carbon dioxide, and (3) the use of alumina as a support for catalysts containing only cobalt results in no, or at best only a slight, increase in activity compared to the use of cobalt on other supports. Thus, for reasons not fully understood, the combination of cobalt and rhenium supported on alumina results in a catalyst which is significantly more active than either of the two individual metals supported on alumina or the combination of the two metals supported on other inorganic supports, such as silica, magnesia, silica-alumina, titania, chromia or zirconia. Furthermore, the product distribution with a high selectivity to C_2+ hydrocarbons and low selectivity to methane and carbon dioxide would not have been predicted based on the known product distribution from rhenium catalysts. In addition, the addition of an alkali to the catalyst serves to increase the average carbon number of the product. This is advantageous in situations where the market value of the lighter products is lower than that of the heavier products.

Broadly, the present invention provides a catalyst for converting synthesis gas to hydrocarbons and a process therefor. The catalyst is characterized in that it comprises catalytically active amounts of cobalt and relatively lesser amounts of rhenium composite on an alumina support.

The process includes the step of contacting a synthesis gas feed comprised of hydrogen and carbon monoxide over a catalyst comprised of cobalt and rhenium composite on an alumina support wherein rhenium is present in relatively lesser amounts than the cobalt content of the catalyst, at a temperature, gaseous hourly space velocity and a pressure useful for promoting a Fischer-Tropsch Synthesis.

Preferably, the reaction conditions include a temperature in the range of about 150 to 325°C, a pressure in the range of about atmospheric to 100 atmospheres and a gaseous hourly space velocity, based on the total amount of synthesis gas feed, in the range of about 100 to 20,000 cm^3 of gas per gram of catalyst per hour. The catalyst used in the process of this invention preferably contains from about 5 to 60% cobalt and has a rhenium content between 0.5 and 50% of the amount of cobalt. The alumina preferably is gamma alumina.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph showing the effect of rhenium content on CO conversion using catalysts containing 12% cobalt;

Figure 2 is a graph showing the effect on CO conversion of adding rhenium to catalysts containing various amounts of cobalt on an alumina support;

Figure 3 is a typical graph of CO conversion as a function of time on stream for the process of this invention when operated using slurry reaction; and

Figure 4 is a gas chromatogram of a typical middle distillate and heavier liquid product from the process of this invention.

Figure 5 is a graph showing the effect of potassium to cobalt ratio on the Schulz-Flory α of the product produced using the catalysts of this invention; and

Figure 6 is a graph showing the effect of potassium to cobalt ratio on CO conversion when using the catalysts of this invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The catalyst of the present invention comprises as the active catalytic ingredients cobalt and rhenium supported on alumina with rhenium present in a relatively smaller amount than cobalt. Optionally, the catalyst can also comprise an alkali metal, that is an element from Group IA of the Periodic Table.

The process of the present invention comprises contacting at reaction conditions a feed comprised of hydrogen and carbon monoxide over a catalyst which comprises as the active catalytic ingredients cobalt and rhenium supported on alumina with rhenium present in a relatively smaller amount than cobalt.

Operating conditions suitable for use in the process of this invention are reaction temperatures between 150 and 300°C, preferably between 180 and 280°C, and more preferably between 190 and 250°C; a total pressure from atmospheric to around 100 atmospheres, preferably between 1 and 40 atmospheres, and more preferably between 1 and 30 atmospheres; and a gaseous hourly space velocity, based on the total amount of synthesis gas feed, between 100 and 20,000 cm^3 of gas per gram of catalyst per hour, and preferably from 100 to 10,000 $cm^3/g/h$, where gaseous hourly space velocity is defined as the volume of gas (measured at standard temperature and pressure) fed per unit weight of catalyst per hour.

The catalyst used in the process of this invention has been found to be highly active for the conversion of synthesis gas, a mixture of hydrogen and carbon monoxide, into a mixture of predominantly paraffinic hydrocarbons. As indicated above, it has long been known that cobalt is an active catalyst for the F-T synthesis. It is also known that the addition of rhenium to a cobalt catalyst supported on titania gives improved activity, even if rhenium by itself shows very low activity for F-T synthesis and produces methane as the main product. Surprisingly, we have found that the choice of support for the cobalt plus rhenium catalyst is very critical, and that the addition of rhenium to an alumina-supported cobalt catalyst gives a much higher improvement in activity than addition of rhenium to cobalt supported on other inorganic oxides. Also, the alkali increases the average carbon number of the product.

The cobalt is added to the alumina support in some amount up to about 60 wt% of the catalyst, including cobalt. Preferably, amounts between 5 and 45 wt% are used; and more preferably between 10 and 45 wt%. The content of rhenium is between about 0.5 and 50 wt% of the cobalt content; preferably between 1 and 30 wt%; and more preferably from about 2 to around 20 wt%. The content of alkali is between about 0.5 and 5 atom % of the cobalt content.

In addition to cobalt, rhenium and alkali, it is beneficial to include a small amount of a metal oxide promoter in an amount between about 0.1 and 5 wt%, and more preferably between about 0.2 and 2 wt%, based on the weight of the complete catalyst. The promoter is suitably chosen from elements in groups IIIB, IVB or VB of the periodic chart, the lanthanides and the actinides. The promoter oxide can be chosen from, for example, Sc_2O_3, Y_2O_3, La_2O_3,

Ce_2O_3, Pr_2O_3, ZrO_2, Ae_2O_3, PaO_2, Nd_2O_3, CaO_3, V_2O_5 or Nb_2O_5. The most preferable oxide is La_2O_3, or a mixture of lanthanides, rich in lanthanum. Oxides like MnO or MgO can also be included. While not essential, the use of these metal oxides is common in the art, since they are believed to promote the production of products with higher boiling points, while maintaining or improving catalytic activity. However, the catalyst is highly active and selective without the addition of one or more of these metal oxide promoters.

The Catalyst Support

The catalytically active metals, the alkali, and the promoter metal oxide, if present, are distended on alumina. Although other supports may be used, it has been found, for example, that silica, titania, chromia, magnesia, silica-alumina and zirconia produce catalysts with much lower activities.

To be most effective when used as a support, alumina should be characterized by low acidity, high surface area, and high purity. These properties are necessary in order to enable the catalyst to have high activity and a low deactivation rate, and to produce high molecular weight hydrocarbon products. The surface area of the alumina support is at least, and preferably greater than, about 100 m^2/g; and more preferably greater than 150 m^2/g. The pore volume is at least, and preferably greater than, about than 0.3 cm^3/g. The catalyst support must be of high purity. That is, the content of elements, e.g. sulfur and phosphorous, that have a deleterious affect on catalytic activity must be kept low. The sulfur content of the catalyst support should be kept below 100 ppa and preferably below 50 ppa. Although gamma alumina has generally been used and is preferred, a number of alumina structures, if prepared properly, can meet these conditions and are suitable supports. For example, eta-alumina, ki-alumina, theta-alumina, delta-alumina, kappa-alumina, boshmite ande pseudo-boehmite can all be used as supports.

Catalyst Preparation

The method of depositing the active metals, the alkali, and the promoter oxide on the alumina support is not critical, and can be chosen from various methods well known to those skilled in the art. One suitable method that has been employed is known as incipient wetness impregnation. In this method the metal salts are dissolved in an amount of a suitable solvent just sufficient to fill the pores of the catalyst. In another method, the metal oxides or hydroxides are co-precipitated from an aqueous solution by adding a precipitating agent. In still another method, the metal salts are mixed with the wet support in a suitable blender to obtain a substantially homogeneous mixture. In the present invention, if incipient wetness impregnation is used, the catalytically active metals and the alkali can be deposited on the support using an aqueous or an organic solution. Suitable organic solvents include, for example, acetone, methanol, ethanol, dimethyl formamide, dimethyl ether, cyclohexane, xylene and tetrahydrofuran. Aqueous impregnation is preferred when $Co(NO_3)_2$ is used as the salt, while an organic solvent is the preferred solvent when the catalyst is prepared from cobalt carbonyl.

Suitable cobalt compounds include, for example, cobalt nitrate, cobalt acetate, cobalt chloride and cobalt carbonyl, with the nitrate being the most preferable when impregnating from an aqueous solution. Suitable rhenium compounds include, for example, rhenium oxide, rhenium chloride and perrhenic acid.

Perrhenic acid is the preferred compound when preparing a catalyst using an aqueous solution.

Suitable alkali salts for incorporating the alkali into the catalyst include, for example, the nitrates, chlorides, carbonates, and hydroxides. The metal oxide promoter can suitably be incorporated into the catalyst in the form, for example, of the nitrate or chloride.

After aqueous impregnation, the catalyst is dried at 110 to 120°C for 3 to 6 hours. When impregnating from organic solvents, the catalyst is preferably first dried in a rotary evaporator apparatus at 50 to 60°C under low pressure, then dried at 110 to 120°C for several hours longer.

The dried catalyst is calcined under flowing air by slowly increasing the temperature to an upper limit of between 200 and 500°C, preferably between 250 and 350°C. The rate of temperature increase is preferably between 0.5 and 2°C per minute, and the catalyst is held at the highest temperature for a period of 2 to 5 hours. The impregnation procedure is repeated as many times as necessary to obtain a catalyst with the desired metals content. Cobalt, rhenium and the promoter, if present, can be impregnated together, or in separate steps. If separate steps are used, the order of impregnating the active components can be varied.

Before use, the calcined catalyst is preferably reduced with hydrogen. This can suitably be done in flowing hydrogen at atmospheric pressure at a flow rate between 30 and 100 cm^3/min when reducing about 2 g of catalyst. The flow rate should suitably be increased for larger quantities of catalyst. The temperature is increased at a rate between 0.5 and 2°C per minute from ambient to a maximum level of 250 to 450°C, preferably between 300 and 400°C, and maintained at the maximum temperature for about 6 to 24 hours, more preferably 10 to 24 hours.

After the reduction step, the catalysts may be oxidized and reduced before use. To carry out the oxidation step, the catalyst is treated with dilute oxygen (1-3% oxygen in nitrogen) at room temperature for a period of 1/2 to 2 hours before the temperature is increased at the same rate and to the same temperature as used during calcination. After holding the high temperature for 1 to 2 hours, air is slowly introduced, and the treatment is continued under air at the high temperature for another 2 to 4 hours. The second reduction is carried out under the same conditions as the first reduction.

Hydrocarbon Synthesis

The reactor used for the synthesis of hydrocarbons from synthesis gas can be chosen from various types well known to those skilled in the art, for example, fixed bed, fluidized bed, ebullating bed or slurry. Because of the exothermic nature of the F-T reaction, the reactor must be designed with heat removal capabilities so that the desired reaction temperature can be carefully controlled. The above listed reactor types have characteristics that make them well suited for use in the process of this invention. The catalyst particle size for the fixed or ebullating bed is preferably between 0.1 and 10 mm and more preferably between 0.5 and 5 mm. For the other types of reactors a particle size between 0.01 and 0.2 mm is preferred.

The synthesis gas used as feed to the process is a mixture of carbon monoxide and hydrogen and can be obtained from any source known to those skilled in the art, such as, for example, steam reforming of natural gas or partial oxidation of coal. The molar ratio of H_2:CO is normally between 0.5 to 3:1; preferably between 1:1 to 3:1; and more preferably between 1.5:1 to 2.5:1. Carbon dioxide is not a desired feed component for use with the process of this invention, but it does adversely affect the process or the activity of the catalyst, other than acting as a diluent. All sulfur compounds must, on the other hand, be held to very low levels in the feed, preferably below 1 ppm, because they have an adverse effect on the activity of the catalyst employed in this process.

The process of this invention is described as follows. Synthesis gas from any suitable source, as discussed previously, is fed to the process. The ratio of hydrogen to carbon monoxide in this synthesis gas may be between 1 and 3 and more preferably between 1.5 and 2.5. A highly desirable ratio is the stoichiometric ratio of H_2 to CO usage within the process, which is about 1.2 to 2.2. Providing syngas at this stoichiometric ratio results in the most efficient utilization of the syngas in the process, since neither hydrogen nor carbon monoxide is in excess. In addition to H_2 and CO, the syngas may contain quantities of other gases, such as carbon dioxide, methane, and nitrogen. These gases act as diluents which may be disadvantageous for some kinds of reactor systems, while being advantageous for other reactor systems, as will be more fully discussed below. The hydrogen sulfide content of the syngas must be kept very low, preferably below 1 ppm by volume, because sulfur is a severe catalyst poison.

If not at sufficient pressure, the syngas is compressed to process pressure, which can be from atmospheric to about 100 atmospheres, preferably from 1 to 40 atmospheres, and more preferably from 1 to 30 atmospheres. Anything lower than 1 atmosphere would require operation at vacuum conditions which is not necessary and unduly expensive. The rate of reaction would decrease. Pressures greater than about 100 atmospheres would increase the cost significantly due to the increased strength of the equipment necessary to withstand high pressures. The syngas is then preheated before entering the reactor. Because the F-T reaction is highly exothermic, it is not normally necessary to heat the feed gas all the way to reaction temperature, the final heatup taking place in the reactor itself. As discussed previously, the reactor can suitably be chosen from a variety of reactor types, the most important criterion being the ability to control carefully the temperature of the exothermic F-T reaction. The three most suitable reactor types are tubular fixed bed reactors, in which the catalyst is placed in tubes and a fluid is circulated on the outside of the tubes for heat removal, fluidized bed reactors, and slurry reactors, in which finely divided catalyst is slurried in a vehicle oil. In these latter two reactor types, heat can be removed in a variety of ways, including increases in the sensible heat of the feed, internal heat exchangers, and removal of a slip stream for cooling and return to the reactor.

Temperature in the reactor should be between 150 and 325°C, and more preferably between 180 and 280°C. The total pressure can be from atmospheres to around 100 atmospheres between 1 and 30 atmospheres. These temperature ranges are typical to Fischer-Tropsch reactions. The rate of reaction at temperatures below 150°C would be so low as to be uneconomical on a commercial scale due to the large reactor size which would be required. Where temperatures above about 325°C are employed, the selectivity to liquid hydrocarbons is so low that the process becomes economically infeasible. There are less expensive ways to make methane. Gaseous hourly space velocity (based only on the H_2 plus CO content of the feed) should be between 0.1 and 20 m^3 per kg catalyst per hour and preferably between 0.1 and 10 m^3 per kg catalyst per hour. Once the desired working temperature and pressure are determined, the space velocity is chosen to give the desired per pass conversion.

The acceptable form of the catalyst will depend upon the type of reactor being used. For tubular fixed bed reactors, the catalyst can be in the form of extrudates, pellets, spheres, granules, etc. with a nominal diameter of about 0.5 to 6 mm, and preferably about 1.5 mm. For fluidized bed or slurry reactors, the catalyst should be in finely divided form. A typical analysis for a catalyst suitable for slurry reactor operation is:

Particle Diameter Microns	Weight % of Sample
0-5	0.2
0.7	1.5
7-9	1.3
9-13	0.5
13.19	1.1
19-27	1.5
27-38	3.3
38-53	5.7
53-75	15.7
75-106	25.7
106-150	26.4
150-212	13.9
212-300	3.2

For either fluidized bed or slurry operation, it is important that the catalyst charge contain neither too large a fraction of large particles nor too large a fraction of small particles. A proper size consist is important for successful fluidization or suspension of the catalyst. In slurry operation, it is also important to have a proper vehicle. Normally, a fraction of the product oil will be used for this purpose. Generally, a carbon number distribution in the range from C_{20} to C_{50} is satisfactory. For startup purposes, in addition to a F-T liquid, C_{30} to C_{50}

poly-alpha-olefins may be used or a highly refined, i.e. heteroatom and aromatic free, petroleum oil.

In the reactor, contact between the syngas and the catalyst results in the production of largely paraffinic hydrocarbons, along with small amounts of olefins and oxygenates. In general, part of the product will remain in the gas phase and be carried out of the reactor along with inerts and unconverted feed gas, and part of the product will form a liquid phase. The fraction of the product that is carried out in the vapour phase will depend upon the operating conditions being used.

In a fixed bed reactor, the liquid phase will either drain out the bottom of the catalyst tubes or else be entrained out with the offgas. In a fluidized bed reactor, operating conditions must be adjusted so that the amount of liquid product is very low. Otherwise, the product builds upon the catalyst and destroys the fluidization properties of the catalyst. In the slurry reactor, the liquid products will dissolve in the vehicle oil and can be recovered by any of the techniques familiar to those skilled in the art, such as filtration, centrifugation, settling and decanting, etc.

The offgas from the reactor is cooled to condense liquid products (both hydrocarbons and water, which is produced as a byproduct). This is typically done in a series of steps at progressively lower temperatures. This is necessary to prevent wax from solidifying and causing plugging. After the final cooler/separator, additional hydrocarbons can be recovered by absorption or adsorption, if desired.

Per pass conversion in the reactor can vary from 10 to over 90%, preferably from 40 to over 90%. If once through conversion is not sufficiently high, the offgas, after product recovery and bleeding off of a slip stream to prevent inerts from building up in the system, can be mixed with the fresh syngas feed and recycled to the reactor.

As mentioned above, the syngas may contain some quantity of nitrogen. For fixed bed operation, this may be undesirable, since dilution with nitrogen reduces the partial pressure of reactive gases and increases the pressure drop. However, for fluidized bed and slurry reactor operation, the nitrogen may be beneficial by providing additional mixing energy and helping keep the catalyst suspended. In these types of reactors, pressure drop is not a strong function of flow rate.

As a final step in the process, all the liquid products may be combined. If desired they may be stabilized by distillation to remove highly volatile components. The liquid product may then be marketed as a synthetic crude or, alternatively, distilled into individual product outs which can be marketed separately. As a further alternative, the product may be catalytically dewaxed or hydrocracked before being marketed. These latter processes can improve product properties by lowering pour point, increasing octane number, and changing boiling ranges.

The products from this process are a complicated mixture, consisting predominantly of normal paraffins, but also containing small amounts of branched chain isomers, olefins, alcohols and other oxygenated compounds. The main reaction can be illustrated by the following equation:

$$nCO + 2nH_2 \dashrightarrow (-CH_2-)_n + nH_2O$$

where $(-CH_2-)_n$ represents a straight chain hydrocarbon of carbon number n. Carbon number refers to the number of carbon atoms making up the main skeleton of the molecule. Products range in carbon number from one to 50 or higher.

In addition, with many catalysts, for example those based on iron, the water gas shift reaction is a well known side reaction:

$$CO + H_2O \dashrightarrow H_2 + CO_2$$

With the catalyst used in the process of this invention, the rate of this last reaction is usually very low. However, it is found that, even though rhenium catalysts exhibit a relatively high selectivity to carbon dioxide, the cobalt plus rhenium catalyst used in the process of this invention surprisingly does not have a higher selectivity to carbon dioxide than the cobalt only catalyst.

The hydrocarbon products from processes employing the Fischer-Tropsch synthesis are generally distributed from methane to high boiling compounds according to the so called Schulz-Flory distribution, well known to those skilled in the art. The Schulz-Flory distribution is expressed mathematically by the Schulz-Flory equation.

$$W_i = (1 - \alpha)^2 i \alpha^{i-1}$$

where i represents carbon number, α is the Schulz-Flory distribution factor which represents the ratio of the rate of chain propagation to the rate of chain propagation plus the rate of chain termination, and Wi represents the weight fraction of product of carbon number i. This equation shows that an increased α results in a higher average carbon number of the products. Higher α values are desirable when heavier products, such as diesel fuel, are relatively more valuable than lighter products, such as naphtha.

The products produced by the catalyst and the process of this invention generally follow the Schultz-Flory distribution, except that the yield of methane is usually higher than expected from this distribution. This indicates that methane is apparently produced by an additional mechanism.

Catalysts promoted with alkali in the manner prescribed in this invention produce a product having a higher average carbon number than the products from non-alkali promoted catalysts. That is, the Schulz-Flory α for the product from an alkali promoted catalyst is higher than for a non-alkali promoted catalyst.

It is well known, and also shown in one of the following examples, that rhenium alone is a low activity catalyst for Fischer-Tropsch synthesis producing a product which is predominantly methane. On the other hand, cobalt is a well known catalyst for producing higher carbon number hydrocarbons. In U.S. Patent No. 4,568,663, it has been shown that adding small amounts of rhenium to cobalt supported on titania improves the catalytic activity. In the present invention, it has been found that the hydrocarbon yield obtained by adding rhenium is surprisingly much larger for an alumina supported cobalt catalyst than that obtained from cobalt and rhenium on several other inorganic supports. The improved activity and increased selectivity to heavier hydrocarbons is followed by no deleterious effect on the selectivity to methane.

The catalyst and the process of this invention is further described in the following examples.

Experimental Work

The following examples describe the preparation of various catalysts and the results obtained from testing these catalysts for conversion of synthesis gas into hydrocarbons.

Before being tested, each catalyst was given a pretreatment consisting of reduction by passing hydrogen over the catalyst at a rate of 3000 $cm^3/g/h$ while heating the catalyst at a rate of 1°C/min to 350°C and maintaining this temperature for 10 hours. In all the process tests except for Example 42, synthesis gas consisting of 33 vol % carbon monoxide and 67 vol hydrogen was passed over 0.5 g of the catalyst in a small fixed bed reactor at atmospheric pressure at temperatures of 185, 195 and 205°C according to the following schedule:

9 hr. 50 min. at 195°C
4 hr. 20 min. at 205°C
4 hr. 30 min. at 185°C
9 hr. 50 min. at 195°C

The flow rate of gas was 1680 cm^3/g of catalyst /h. Products from the reactor were sent to a gas chromatograph for analysis. Catalysts were compared based on the results over the period from 10 to 30 hours on stream.

EXAMPLE 1

Catalyst Containing Cobalt But No Rhenium

This example describes the preparation of a control cobalt catalyst which was used for comparative purposes. This catalyst was prepared as follows:

A solution was prepared by dissolving 17.03 g of cobalt nitrate, $Co(NO_3)_2.6H_2O$, and 0.76 g of mixed rate earth nitrate, $RE(NO_3)_3$, where RE stands for rare earth with a composition of 66% La_2O_3, 24% Nd_2O_3, 8.2% Fr_6O_{11}, 0.7 CeO_2, and 1.1% other oxides (Molycorp 5247), in 30 ml of distilled water. The total solution was added with stirring to 25 g of Ketjen CK300 gamma-alumina which had been calcined 10 hours at 500°C. The prepared catalyst was then dried for 5 hours in an oven at a temperature of 115°C. The dried catalyst was then calcined in air by raising its temperature at a heating rate of 1°C/minute to 300°C and holding at this temperature for 2 hours. The finished catalyst contained 12 wt% cobalt and 1 wt% rare earth oxide with the remainder being alumina. This catalyst is referred to as preparation "a" in Table I. The above procedure was repeated to produce preparation "b" catalyst in Table I.

The results of the tests with this catalyst are shown in Table I. In this and the following tables, selectivity is defined as the percent of the carbon monoxide converted that goes to the indicated product.

Table I

Temp. °C	Preparation	CO Conversion %	C_2+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
185	a	7	91.1	7.2	1.7
	b	11	91.8	7.1	1.1
195	a	12	90.0	8.9	1.1
	b	18	90.2	9.0	0.8
205	a	21	87.7	11.3	1.0
	b	29	86.7	12.4	0.9

This example shows that a cobalt catalyst exhibits good selectivity to ethane and longer chain length hydrocarbons and low selectivity to methane and carbon dioxide.

EXAMPLE 2

Catalyst Containing Rhenium But No Cobalt

This example describes a rhenium catalyst prepared for comparative purposes. The procedure employed was the same as for Example 1 except that the solution contained 0.33 g of perrhenic acid, $RReO_4$ as 82.5% aqueous solution, and 0.54 g of rare earth nitrate to make 24 ml of solution which then was added to 20 g of calcined alumina. The finished catalyst contained 1 wt% rhenium and 1 wt% rare earth oxide with the remainder being alumina.

The results of the tests with the catalyst of Example 2 are shown in Table II.

Table II

Temp. °C	CO Conversion %	C_2+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
185	0.3	20	30	50
195	0.3	19	31	50
205	0.3	19	31	50

EXAMPLE 3

Catalyst Containing Rhenium But No Cobalt

Repetition of the procedure from Example 3, except that 0.83 g of perrhenic acid were used, gave a catalyst containing 4 wt% rhenium. The results of the tests with the catalyst of Example 3 are shown in Table III.

Table III

Temp. °C	CO Conversion %	C_2+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
185	0.3	20	30	50
195	0.3	19	31	50
205	0.3	19	31	50

The results from Examples 2 and 3 show that catalysts containing rhenium but no cobalt have very low activity for producing desirable liquid hydrocarbons from synthesis gas. Furthermore, about half the product is carbon dioxide, and most of the hydrocarbon product is methane.

EXAMPLES 4 THROUGH 11

Catalysts Containing Both Cobalt and Rhenium

The preparation procedure of Example 1 was employed except that varying amounts of perrhenic acid were added to the solution. This produced a series of catalysts containing 12 wt% cobalt and 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, 4.0, and 8.0 wt% rhenium in addition to 1.0 wt% rare earth oxide.

The results of the tests with the catalysts of Examples 4 through 11 at 195°C are shown in Table IV and further illustrated in Figure 1. Figure 1 shows the effect on carbon monoxide conversion of adding rhenium to catalysts containing 12% cobalt.

Table IV

Example No.	Co wt%	Re wt%	CO Conversion %	C_2+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
4	12	0.1	26	89.8	9.6	0.6
5	12	0.2	29	88.9	10.4	0.7
6	12	0.3	27	88.2	11.0	0.8
7	12	0.5	31	88.3	10.9	0.8
8	12	1.0	33	87.7	11.4	0.9
9	12	2.0	31	85.7	13.3	1.0
10	12	4.0	28	84.7	14.2	1.1
11	12	8.0	25	84.5	14.2	1.3

As can be seen from comparison of the results of Table I with Table IV and Figure 1, the addition of small amounts of rhenium to a cobalt supported on alumina catalyst significantly increases the conversion of the carbon monoxide in the feed. Levels of rhenium as low as 0.1 wt%

result in approximately doubling the CO conversion. The exact level of Re for optimum activity is very important, as the rate of carbon monoxide conversion increases rapidly at low rhenium addition levels, reaches a maximum and then decreases gradually at levels greater than 1 wt% rhenium. However, even at the highest rhenium level investigated (8%), a clear improvement in conversion is evident when compared to the catalyst not containing rhenium.

It is important that the increase in activity occur without a corresponding increase in either the methane or the carbon dioxide selectivities. Table IV shows that the increase in carbon monoxide conversion is not accompanied by any substantial change in either the selectivities to methane or carbon dioxide. Thus, after rhenium addition the principal reaction products are still desirable hydrocarbons.

EXAMPLES 12 THROUGH 25

Catalysts Containing Both Cobalt and Rhenium

The preparation procedure of Example 1 was employed except that varying amount of cobalt nitrate and perrhenic acid were added to the solution. This produced a series of catalysts containing from 3.0 to 40 wt% cobalt and from 0 to 5.0 wt% rhenium in addition to 1.0 wt% rare earth oxide.

The results of the tests with the catalysts of Examples 12 through 25 at 195°C are shown in Table V.

Table V

Example No.	Co wt%	Re wt%	CO Conversion %	C_2+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
12	3	0.0	5	90.7	8.1	1.2
13	3	0.25	4	87.2	10.4	2.4
14	6	0.0	12	90.0	8.9	1.1
15	6	0.5	16	88.2	10.8	1.0
16	9	0.0	15	90.0	9.1	0.9
17	9	0.75	25	88.1	11.1	0.8
18	20	0.0	20	89.3	9.8	0.9
19	20	0.5	40	87.9	11.1	1.0
20	20	1.0	46	86.1	12.9	1.0
21	20	5.0	42	83.9	14.8	1.3
22	40	0.0	20	89.3	9.7	1.0
23	40	1.0	56	85.0	13.2	1.8
24	40	2.0	58	84.3	13.7	2.0
25	40	5.0	60	81.9	15.7	2.4

The results in Table V show that for cobalt catalysts without rhenium, there is a significant increase in activity in going from 3% cobalt to 6% cobalt. However, only modest increases in activity occur from this point up to cobalt loadings of as high as 40%. At a cobalt loading of 3%, the addition of rhenium does not improve the catalytic activity, but the improvement upon rhenium addition is significant for higher cobalt loadings. In fact, the improvement in activity due to the addition of rhenium increases as the cobalt content increases as shown in Figure 2.

EXAMPLES 26 AND 27

Cobalt/Rhenium Catalysts with Promoters

To illustrate the use of promoters other than rare earth oxides, the following catalysts were prepared. The preparation procedure used to prepare the catalyst of Example 8 was used except that zirconium nitrate, $Zr(NO_3)_4$, or vanadyl oxalate, $VO(C_2O_4H)_3$, was substituted for the rare earth nitrate. The results of tests at 195°C with the catalysts of examples 26 and 27 are shown in Table VI. In addition to the promoter, these catalysts contained 12% cobalt and 1% rhenium and were supported on alumina.

Table VI

Example No.	Promoter	CO Conversion %	C_2+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
26	ZrO_2 (0.75 wt%)	31	87.9	11.3	0.8
27	V_2O_5 (0.56 wt%)	26	89.4	9.8	0.8

EXAMPLES 28 THROUGH 41

Cobalt/Rhenium Catalysts On Other Supports

For comparison with alumina, several catalysts were prepared on other supports. The preparation procedure used to prepare the catalyst of Example 8 was repeated, but without the addition of rare earth oxide. The titanium-supported catalysts were prepared on titania calcined at both 500°C and 600°C. After calcination at 600°C, the titania is mainly in the crystalline rutile form; while after calcination at 500°C the anatase; rutile ratio is about 1:1. The catalysts prepared on the titania support calcined at these two temperatures showed exactly the same catalytic activity.

The supports used were: Davison Grade 59 silica; Degussa P25 titania; Alpha Chemicals No. 88272 chromia; magnesia prepared by calcining Fischer basic magnesium carbonate; American Cyanamid AAA Silica-Alumina; and Alpha Chemicals 11852 zirconia (containing 2% alumina). Information on the composition of the catalysts prepared on the different supports is given in Table VII.

Table VII

Example No.	Support	Weight of Support g	Weight of Materials in Impregnating Solution, g		Composition of Finished Catalyst, wt%	
			$Co(NO_3)_2$	$HReO_4$*	Co	Re
28	Silica	20	13.47	-	12	-
29	Silica	20	13.62	0.38	12	1.0
30	Titania **	25	16.84	-	12	-
31	Titania **	24.64	16.78	0.46	12	1.0
32	Titania ***	25	16.84	-	12	-
33	Titania ***	24.64	16.78	0.46	12	1.0
34	Chromia	20	13.47	-	12	-
35	Chromia	21.3	14.51	0.40	12	1.0
36	Magnesia	21.59	14.54	-	12	-
37	Magnesia	14.54	10.67	0.29	12	1.0
38	Silica-Alumina	20	13.47	-	12	-
39	Silica-Alumina	20	13.62	0.38	12	1.0
40	Zirconia	20	13.47	-	12	-
41	Zirconia	20	13.62	0.38	12	1.0

*	Weight of 82.5% perrhenic acid solution
**	Calcined at 500°C
***	Calcined at 500°C

A series of tests was conducted to evaluate the activities of the catalysts of the above examples in converting synthesis gas into hydrocarbons. The results of the tests with the catalysts of Examples 28 through 41 at 195°C are shown in Table VIII. The results from catalysts prepared on alumina are included for comparison.

Table VIII

Ex. No.	Co %	Re %	Support	CO Conversion %	C_2+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
1	12	-	Al_2O_3	12	90.0	8.9	1.1
8	12	1	Al_2O_3	33	87.7	11.4	0.9
28	12	-	SiO_2	11	90.1	8.7	1.2
29	12	1	SiO_2	12	88.1	10.7	1.2
30	12	-	TiO_2*	11	87.6	11.8	0.6
31	12	1	TiO_2*	17	86.5	12.8	0.7
32	12	-	TiO_2**	11	87.6	11.7	0.7
33	12	1	TiO_2**	17	85.8	13.5	0.7
34	12	-	Cr_2O_3	1	83.5	15.5	1.0
35	12	1	Cr_2O_3	2	80.8	12.3	6.9
36	12	-	MgO	0.3	20.0	30.0	50.0
37	12	1	MgO	0.3	19.1	30.9	50.0
38	12	-	SiO_2/ Al_2O_3	5	76.3	22.2	1.5
39	12	1	SiO_2/ Al_2O_3	6	78.6	19.8	1.6
40	12	-	ZrO_2	4	80.9	16.3	2.8
41	12	1	ZrO_2	7	78.8	18.7	2.5

* Support calcined at 500°C
** Support calcined at 600°C

The catalysts in Table VII were prepared to test the teaching that various inorganic supports are acceptable for preparing cobalt plus rhenium F-T catalysts. An examination of the data in Table VIII leads to the surprising conclusion that the type of support is extremely important and that vast differences in activity exist between catalysts prepared on one support and catalysts of the same catalytic metals content on another support. More surprisingly, only cobalt plus rhenium on alumina showed a commercially attractive activity level and selectivity.

Catalysts on magnesia and chromia exhibited extremely low activities, both with and without rhenium. Catalysts on zirconia and silica-alumina showed somewhat higher activities, but selectivity to C_2+ hydrocarbons was poor. These catalysts showed only modest improvements in activity upon the addition of rhenium.

Catalysts without rhenium supported on silica and titania showed activity levels close to comparable cobalt on alumina catalyst. However, upon addition of rhenium, the alumina catalyst showed a surprising increase in activity from about 15% carbon monoxide conversion to 33% carbon monoxide conversion; whereas, the silica supported catalyst showed only a very small increase in activity from 11% carbon monoxide conversion to 12% carbon monoxide conversion, while the titania supported catalyst showed a larger, but still modest, gain in activity from 11% carbon monoxide conversion to 17% carbon monoxide conversion.

From these examples, plus those presented previously, it can be concluded that the catalytic activity of a cobalt catalyst supported on alumina is greatly improved by adding minor amounts of rhenium, as long as the cobalt level is greater than about 5 wt%. Although improved activity from rhenium addition is also observed for some other supports, the activity level achieved by adding rhenium to a catalyst supported on alumina is much higher than for other supports. This result is surprising and would not have been predicted based on teachings in the prior art.

EXAMPLE 42

A catalyst was prepared according to the procedure of Example 24, except that Harshaw 4100P alumina was used as the support. Before being tested in a slurry reactor, the catalyst was pretreated as follows. One hundred grams of this catalyst was loaded into a vertical pipe pretreating reactor constructed of 5 ft. of 1 in. OD schedule 40 stainless steel pipe. Hydrogen was introduced to the bottom of the pipe reactor at a rate of 1900 sec/min., which was sufficient to fluidize the catalyst in the pretreating reactor. After a fluidized bed was established, temperature was increased at the rate of 1°C/min. to a maximum of temperature of 350°C. The catalyst was held at this temperature for 16 hr. and then cooled at 50°C. At this point, the hydrogen was replaced with He, and the catalyst was cooled to ambient temperature. 14.1 g of this reduced catalyst were mixed with 206 grams of Synfluid (Synfluid* 8 cSt PAO, Chevron Chemical Company) and loaded into a 1 in. ID by 3 ft. long slurry reactor. A mixture of CO, H_2, and N_2

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* Trade-mark

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in a ratio of 1:2:3 was fed to the reactor at a rate of 1080 sl/hr. Temperature was increased to 225°C and pressure was increased to 450 psig (approximately 31 atmospheres). These conditions were maintained for a total of 388 hours, except for two periods, one of 68 hours and the other 94 hours during which pure N_2 was fed to the reactor. After a transition period of 2 hours, there then followed a period of 90 hours during which the ratio of $CO:H_2:N_2$ in the feed was 1:3:4. There then followed a period of 53 hours during which operation was unstable due to problems with temperature control. During this period some high temperatures were experienced, followed by a short period of no activity from which the catalyst quickly recovered. It is postulated that during the high temperature period, an abundance of light hydrocarbons were formed which diluted the vehicle liquid and caused collapse of the slurry bed. This illustrates the importance of maintaining the proper vehicle properties, mixing energy, etc. It also illustrates the inherent ruggedness of the process, since it was able to recover from this incident. This was followed by 160 hours which the ratio of $CO:H_2:N_2$ in the feed was 1:1:2. After a 7 hours transition period, this was followed by a period of 115 hours in which the ratio of $CO:H_2:H_2$ in the feed was again 1:2:3. After a 9 hour transition period, there then followed a period of 157 hours with a $CO:H_2:N_2$ ratio in the feed gas of 2:3:5. Finally, after a 5 hour transition period, there was a period of 94 hours with a $CO:H_2N_2$ feed ratio of 2:5:7. Altogether from startup to shutdown, the run lasted 1080 hours.

Figure 3 is a graph of CO conversion as a function of time on stream. This graph demonstrates the stability of the process and shows that the rate of deactivation is low. during operation, product was removed continuously from the unit, so that the slurry volume in the reactor remained constant. Figure 4 is a gas chromatogram of a sample of the middle distillate and heavier liquid product. The product is predominantly normal paraffins with a typical Schulz-Flory distribution, showing that the catalyst is promoting the Fischer-Tropsch reaction.

This example demonstrates that the catalyst of this invention is active for the Fischer-Tropsch process. Moreover, it shows that the catalyst may be used in a slurry reactor, as well as in a fixed bed reactor, as illustrated by the previous examples.

EXAMPLES 43 THROUGH 57

Catalyst Containing Cobalt, Rhenium, and Alkali

To demonstrate the advantages of including an alkali in the catalysts of this invention, the catalysts of Examples 43 through 55 were prepared and tested.

The catalysts of Examples 43 to 51 were prepared on Harshaw Al 4100P alumina which had been screened to 100-270 mesh. The catalysts of Examples 52 to 57 were prepared on Ketjen CK300 gamma alumina, screened to 20-40 mesh. Both supports were calcined overnight at 500°C before use. The technique used for preparing the catalysts was incipient wetness, as described in Example 1. The amounts of materials used in the preparation of each catalyst are shown in Table IX. The prepared catalysts were then air dried for

5 to 24 hours in an oven at a temperature of 120°C. The dried catalysts were then calcined in air by raising the temperature at a heating rate of 1°C/minute to 300°C and holding at this temperature for 2 to 16 hours. The compositions of the finished catalysts are shown in Table IX.

The results from testing these catalysts are shown in Table X. As is clear from these results, the addition of an alkali to the catalyst serves to increase the average molecular weight of the product, as evidenced by an increase in the Shultz-Flory α. Higher levels of the alkali result in higher α's as illustrated in Figure 5. However, activity decreases as the alkali content increases, as illustrated in Figure 6. Therefore, for any particular situation there is an optimum alkali level that balances desired average product molecular weight and catalyst activity. Also, the effectiveness of the alkali varies from one alkali to another with, for example, potassium being more effective than lithium.

Table IX

Ex. No.	Wt of Al_2O_3, g	Type of Alkali	Weight of Material in Impregnation Solution, g				Composition of Finished Catalyst wt%			
			(a)	(b)	(c)	(d)	Co	Re	REO	Alkali
43	300.0	-	1039.65	17.21	13.99	-	40	2.0	1.0	0.0
44	75.0	K	260.46	4.31	3.50	0.34	40	2.0	1.0	0.1
45	75.0	K	256.36	4.25	-	0.67	40	2.0	-	0.2
46	175.0	K	609.03	10.08	8.20	1.59	40	2.0	1.0	0.2
47	100.0	K	349.50	5.79	4.70	1.83	40	2.0	1.0	0.4
48	100.0	K	354.03	5.86	4.76	4.64	40	2.0	1.0	1.0
49	60.0	Na	205.49	3.40	-	0.93	40	2.0	-	0.24
50	60.0	Cs	209.55	3.47	-	2.12	40	2.0	-	1.36
51	65.0	Rb	225.38	4.23	-	1.71	40	2.0	-	0.87
52	20.0	-	13.78	0.38	0.62	-	12	1.0	1.0	-
53	20.0	K	13.80	0.38	0.62	0.06	12	1.0	1.0	0.1
54	20.0	Li	13.64	0.38	-	0.11	12	1.0	-	0.05
55	20.0	Li	13.80	0.38	0.62	0.12	12	1.0	1.0	0.05
56	20.0	Cs	13.67	0.38	-	0.10	12	1.0	-	0.3
57	20.0	Cs	13.83	0.38	0.62	0.62	12	1.0	1.0	0.3

(a) $Co(NO_3)_2.6H_2O$

(b) 82.5% $HReO_4$ solution, except for Example 50 which was 72.9% $HReO_4$

(c) Rare earth nitrates (see Example 1)

(d) $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$ or $CsNO_3$

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Table X

Example No.	Alkali		CO Conversion %	CH_4 Selectivity %	Product alpha*
	Type	Content, wt%			
43	-	-	52.5**	14.2**	0.75**
44	K	0.1	52 50	8.6 11.1	0.86 0.79
45	K	0.2	43	9.3	0.83
46	K	0.2	51 44 41	9.5 11.6 9.4	0.84 0.84 0.81
47	K	0.4	30 35	7.3 7.8	0.87 0.85
48	K	1.0	12 9 6	7.0 7.9 6.2	0.88 0.85 0.87
49	Na	0.24	21	8.3	0.82
50	Cs	1.36	14	8.5	0.86
51	Rb	0.87	11	7.3	0.86
52	-	-	31.7***	10.9***	0.77***
53	K	0.1	19 22	7.6 9.8	0.78 0.84
54	Li	0.05	31	11.7	0.78
55	Li	0.05	27	12.0	0.78
56	Cs	0.3	21	11.1	0.83
57	Cs	0.3	21	10.3	0.84

* Calculated by plotting $\ln(W_n/n)$ vs. n, where n is carbon number and W_n is the weight fraction of the product having a carbon number n, and determining the slope of the line.

** Average of 21 tests

*** Average of 6 tests

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A catalyst for converting synthesis gas to hydrocarbons characterised in that it comprises catalytically active amounts of cobalt and relatively lesser amounts of rhenium composited on an alumina support.

2. A catalyst as claimed in claim 1, characterised in that cobalt is present in an amount ranging from 5 to 60 weight percent of the catalyst.

3. A catalyst as claimed in claim 1, characterised in that the cobalt is present in an amount ranging from 10 to 40 weight percent of the catalyst.

4. A catalyst as claimed in any of claims 1, 2 or 3, characterised in that the rhenium is present in an amount ranging from about 0.5 to 50 weight percent of the cobalt content of the catalyst.

5. A catalyst as claimed in any of claims 1, 2 or 3, characterised in that the rhenium is present in an amount ranging from about 1 to 30% of the cobalt content of the catalyst.

6. A catalyst as claimed in claim 1, characterised by comprising an effective amount of an alkali metal promoter.

7. A catalyst as claimed in claim 6, characterised in that the alkali metal promoter is present in a smaller amount than the cobalt content of the catalyst preferably in amounts ranging from 0.5 to 5 atom percent of the cobalt content of the catalyst.

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8. A catalyst as claimed in claim 6, characterised in that the alkali metal promoter is present in amounts ranging from 0.5 to 5 atom percent of the cobalt content of the catalyst.

9. A catalyst as claimed in claim 6, or claim 7, characterised in that the alkali is incorporated into the catalyst as a salt selected from the groups consisting of nitrates, chlorides, carbonates and hydroxides.

10. A catalyst as claimed in claim 1, characterised in that the support has surface area of at least $100m^2/g$ or $150m^2/g$ and a pore volume of at least $0.3cm^3/g$.

11. A catalyst as claimed in claim 1, characterised by comprising an effective amount of a metal oxide promoter comprising an element selected from group III B, IV B or V B of the periodic table, including the lanthanides and the actinides, MgO, or MnO or mixtures thereof.

12. A catalyst as claimed in claim 11, characterised in that the metal oxide promoter is present in an amount ranging from 0.1 to 5 weight percent of the catalyst.

13. A catalyst as claimed in claim 1, for converting synthesis gas to hydrocarbons, characterised in that it comprises cobalt; rhenium and an alkali metal promoter composited on an alumina support wherein cobalt is present in catalytically active amounts up to about 60% of the catalyst, rhenium is present in amounts from about 0.5 to 50 weight percent of the cobalt content of the catalyst and the alkali is present in amounts from about

0.5 to 5 atom percent of the cobalt content of the catalyst.

14. A catalyst as claimed in claim 13, further comprising an effective amount of a promoter selected from the group consisting of oxides of the elements chosen from Groups III B or IV B and V B of the periodic table, the lanthanides and actinides, MgO and MnO and mixtures thereof.

15. A catalyst as claimed in claim 1, characterised in that the support is gamma alumina.

16. A catalyst as claimed in claim 1, characterised in that the sulfur content of the alumina support is kept to levels below about one hundred part per million.

17. A process for the production of hydrocarbons comprising the step of contacting a synthesis gas feed comprised of hydrocarbon and carbon monoxide over a catalyst comprised of cobalt and rhenium composited on an alumina support wherein rhenium is present in relatively lesser amounts than the cobalt content of the catalyst, at a temperature, gaseous hourly space velocity and a pressure useful for promoting a Fischer-Tropsch Synthesis.

18. The process recited in claim 17, wherein the temperature is in the range of about 150° to 325°C.

19. The process recited in claim 17, wherein the pressure is in the range of about 1 to 100 atmospheres.

20. The process recited in claim 17, wherein the gaseous hourly space velocity is in the range of about 0.1 to 50 m^3 of synthesis gas per kilogram of catalyst per hour is employed.

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21. The process recited in claim 17, wherein the cobalt is present in catalytically active amounts up to about 60 weight percent of the catalyst.

22. The process recited in claim 17, wherein the rhenium is present in amounts from about 0.5 to 50 weight percent of the cobalt content of the catalyst.

23. The process recited in claim 17, wherein the alumina is gamma alumina.

24. The process recited in claim 17, wherein the synthesis gas feed is heated before contacting the catalyst.

25. The process recited in claim 17, wherein the contacting step takes place in a fixed bed reactor.

26. The process recited in claim 17, wherein the contacting step takes place in a fluidized bed reactor.

27. The process recited in claim 17, wherein the contacting step takes place in an ebullating bed reactor.

28. The process recited in claim 17, wherein the contacting step takes place in a slurry reactor.

29. The process recited in claim 17, wherein the molar ratio of hydrogen to carbon monoxide is between 0.5:1 to 3:1.

30. The process recited in claim 17, wherein the molar ratio of hydrogen to carbon monoxide is between 1.5:1 to 2.5:1.

31. The process recited in claim 17, further comprising the step of cooling the gaseous product of the contacting step to condense a liquid by exposure to progressively lower temperatures.

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32. The process recited in claim 17, wherein the catalyst is further comprised of a metal oxide promoter chosen from the group consisting of elements in Groups III B, IV B and V B of the periodic chart, the lanthanides and the actinides.

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Fig. 1.

Effect of Rhenium on CO Conversion
Catalysts Containing 12% Cobalt

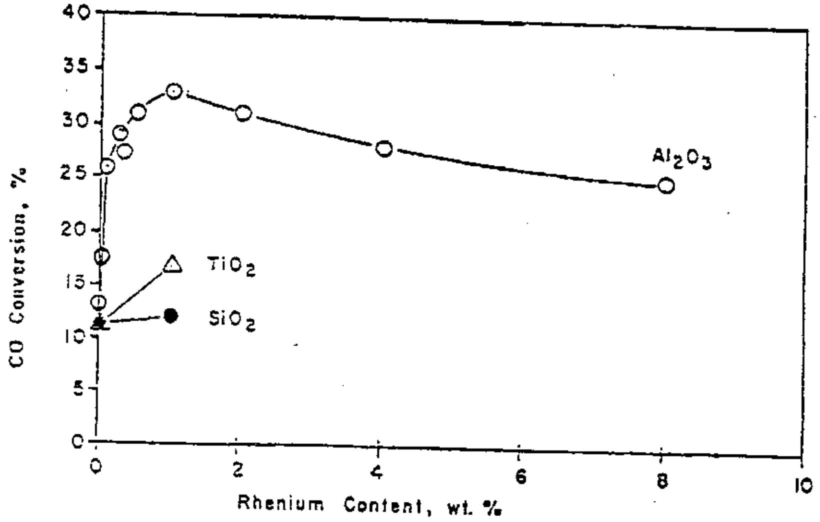

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Fig. 2.

Effect on Conversion of Adding Rhenium to Cobalt on Alumina Catalyst.

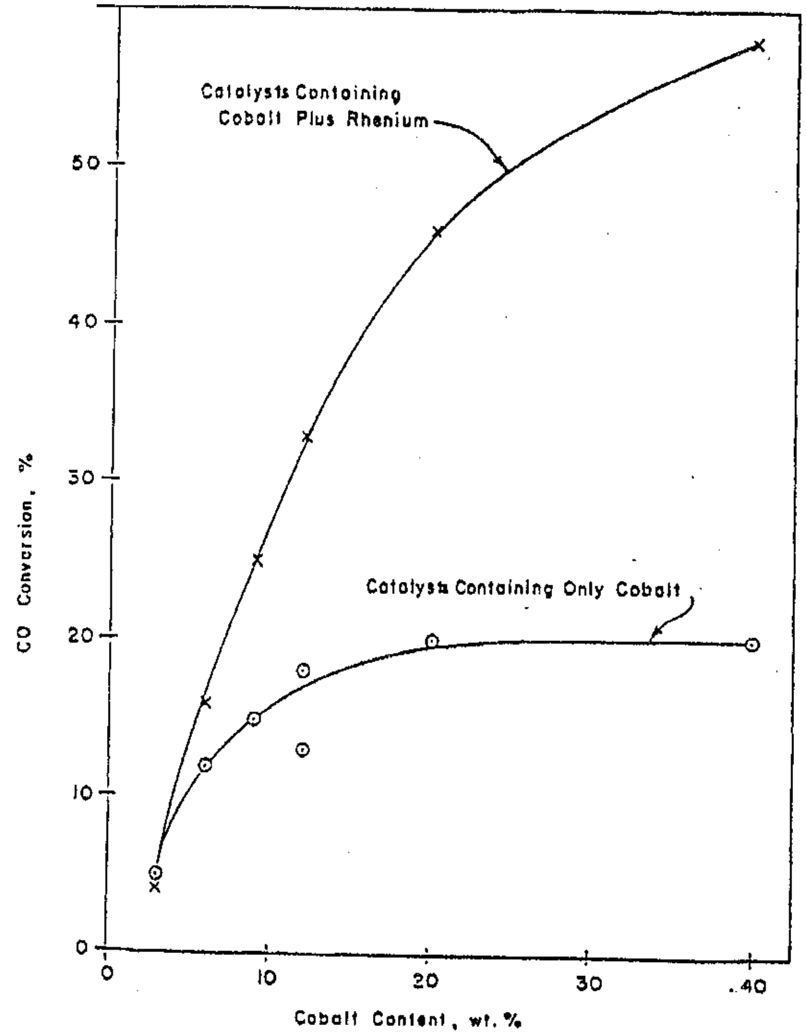

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Fig.3.

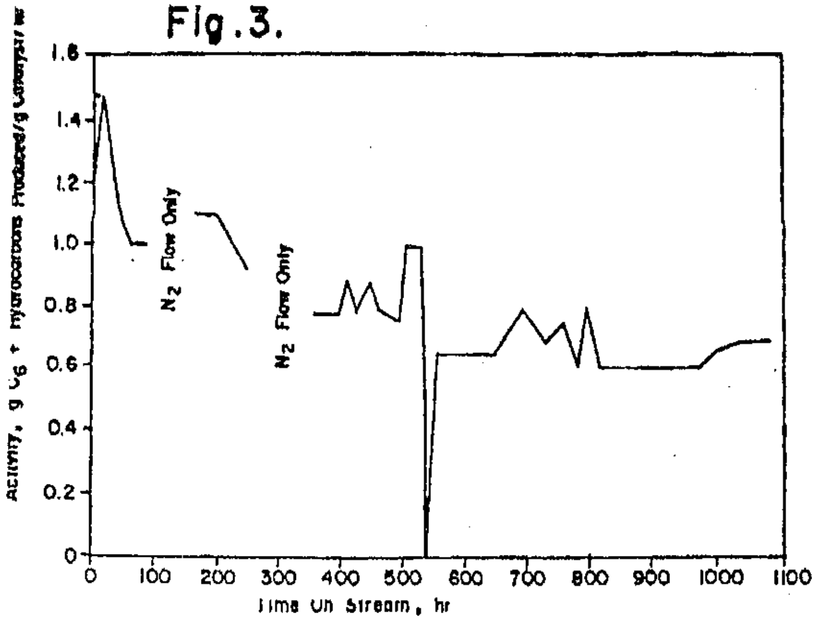

Fig.4.

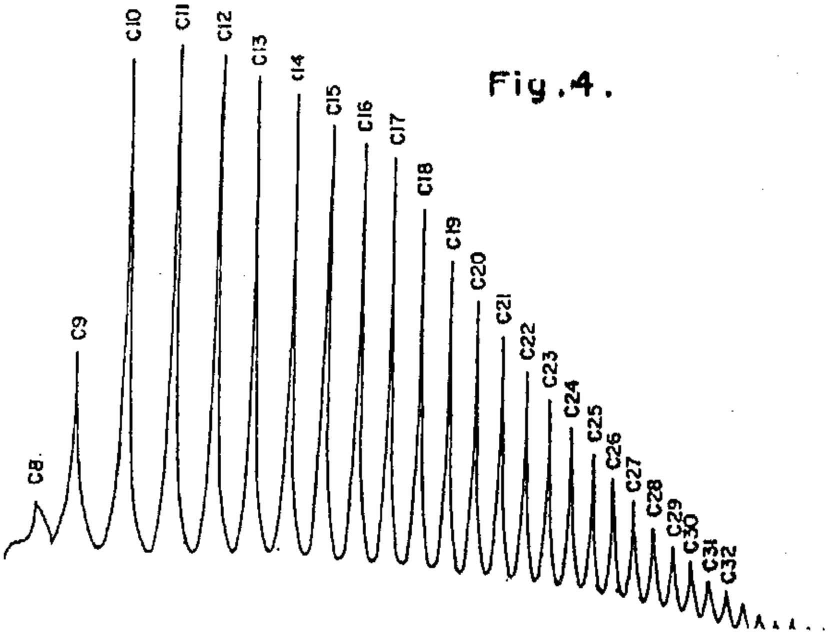

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Figure 5

ALPHA vs. K/Co

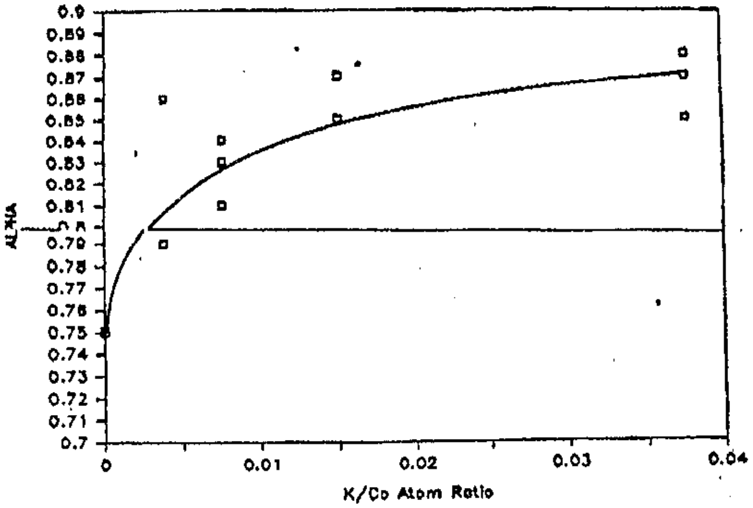

Figure 6

% CO Conversion vs. K/Co