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(54) Title: PREPARATION OF CATALYSTS AND USE THEREOF FOR FISCHER-TROPSCH HYDROCARBON SYNTHESIS

(57) Abstract: Catalysts useful for Fischer-Tropsch hydrocarbon synthesis are prepared by adding an aqueous solution of a carbon-  
ate salt to an aqueous solution of one or more catalytic metal component salts, under mixing conditions, to form a slurry containing  
a hydroxy metal carbonate precipitate of the catalytic metal. This slurry is heated to drive off CO<sub>2</sub> and change the nature of the  
hydroxy metal precipitate and form a second precipitate which is composited with the zeolite component of the catalyst. The com-  
posite, which may also contain promoter metals and other components, is dried to a moisture content of from 6 to 15 wt. % and then  
reduced in hydrogen to form the catalyst.

WO 01/26810 A1

## PREPARATION OF CATALYSTS AND USE THEREOF FOR FISCHER-TROPSCH HYDROCARBON SYNTHESIS

FIELD OF THE INVENTION

The invention relates to the preparation and use of catalysts containing a zeolite component, which are useful for Fischer-Tropsch hydrocarbon synthesis. More particularly, the invention relates to preparing a hydrocarbon synthesis catalyst and a hydrocarbon synthesis process employing the catalyst, wherein the catalyst is formed by a process which comprises precipitating a catalytic metal component in aqueous media with a carbonate, with the resulting slurry heated to drive out CO<sub>2</sub> and form a CO<sub>2</sub>-reduced slurry comprising the precipitate, followed by compositing the precipitate with a zeolite component to form a catalyst precursor, which is then dried and reduced, to form the catalyst.

BACKGROUND OF THE DISCLOSURE

The synthesis of hydrocarbons from a synthesis gas comprising a mixture of H<sub>2</sub> and CO is well known. The synthesis gas feed is contacted with a particulate Fischer-Tropsch type of catalyst at conditions effective for the H<sub>2</sub> and CO in the feed gas to react and form hydrocarbons. The reaction is conducted in a fixed or fluidized catalyst bed reactor or in a slurry reactor. The catalysts are also well known and typically include a composite of at least one iron group catalytic metal component composited with at least one inorganic refractory metal oxide material, such as alumina, amorphous, silica-alumina and the like. Various catalyst preparation methods have been used to form hydrocarbon

- 2 -

synthesis catalysts. For example, US patent 2,850,515 discloses a Fischer-Tropsch catalyst prepared by immersing a dehydrated, acid-refined clay into a metal precipitate, formed by adding an aqueous solution comprising cobalt and magnesium nitrates to an aqueous solution of sodium carbonate. The resulting impregnate is dried and reduced in hydrogen prior to use. US 3,013,990 discloses a hydrogenation catalyst preparation in which a zeolite is ion exchanged with iron, cobalt or nickel, then reduced in hydrogen, followed by heating to dehydrate the composite to form an activated catalyst. US 4,086,262 discloses a hydrocarbon synthesis having a zeolite component, wherein the zeolite, in either an ammonium or ion-exchanged form, is either composited or impregnated with one or more catalytic metal components, and then calcined prior to use. The present conventional method of catalyst preparation for a Fischer-Tropsch catalyst is to composite the catalytic metal component with a zeolite by ion exchange, impregnation or from a molten salt, after which the resulting composite is reduced and calcined or reduced, calcined and reduced again, to form the active catalyst. For example, US patent 4,492,774 discloses preparing a Fischer-Tropsch catalyst by impregnating a zeolite with a catalytic metal salt, followed by drying and calcining. The impregnation-drying and calcining cycle is repeated a multiple number of times, until the desired amount of catalytic metal loading is achieved. The final calcined composite is then activated by a cycle of reduction-oxidation-reduction, to form the activated catalyst.

## SUMMARY OF THE INVENTION

The invention relates to the preparation and use of catalysts useful for synthesizing hydrocarbons from a synthesis gas comprising a mixture of  $H_2$  and CO, such as Fischer-Tropsch hydrocarbon synthesis catalysts, and to their use for synthesizing hydrocarbons. These catalysts are prepared by a process which

- 3 -

comprises (i) precipitating, with a carbonate ion precipitant under mixing conditions, at least one catalytic metal component as a hydroxy metal carbonate, from a catalytic metal salt solution in aqueous media, to form a first slurry (ii) heating the first slurry to remove CO<sub>2</sub> and form a CO<sub>2</sub>-reduced second slurry, in which the hydroxy metal carbonate precipitate is different from that formed in step (i) above, (iii) compositing the precipitate from the second slurry with a zeolite component to form a catalyst precursor, which is then (iv) reduced to form the catalyst. Driving off the CO<sub>2</sub> alters the structure of the precipitated catalytic metal component, so that its structure is different after CO<sub>2</sub> removal, from what it was before CO<sub>2</sub> removal. The precursor is dried prior to reduction and preferably dried to a moisture content of no less than 6 wt. % moisture. More preferably the precursor will have a moisture content of from 6-15 wt. % and most preferably from 8-12 wt. %, prior to reduction. The dry precursor is reduced with hydrogen or a hydrogen-containing reducing gas to form the catalyst. The one or more zeolite components of the catalyst are preferably dehydrated prior to being composited with the catalytic metal precipitate resulting after the CO<sub>2</sub> removal. When used in a Fischer-Tropsch type of hydrocarbon synthesis process, these catalysts have been found to have excellent stability and activity maintenance, with high CO conversion and C<sub>5+</sub> hydrocarbon yield.

The structure of a hydroxy metal carbonate precipitate resulting from using a carbonate ion precipitant, and the catalytic properties of a catalyst derived therefrom, are highly influenced by the exact procedure used to form the catalytic metal precipitate. In the process of forming the catalyst according to the practice of the invention, a carbonate ion precipitant is added to an aqueous solution of at least one catalytic metal salt, to precipitate the catalytic metal as a first hydroxy metal carbonate and form a first slurry, followed by heating the slurry to remove CO<sub>2</sub> and form a CO<sub>2</sub>-reduced, second slurry containing a

- 4 -

second hydroxy metal carbonate. The second hydroxy metal carbonate is different from that which existed prior to the CO<sub>2</sub> removal. The zeolite component(s) of the catalyst is composited with the precipitate after the CO<sub>2</sub> removal, to form the catalyst precursor, which is then dried and reduced as above, to form the catalyst. The catalyst is then loaded into a hydrocarbon synthesis reactor for synthesizing hydrocarbons. In the embodiment in which the catalyst is used for hydrocarbon synthesis, the process comprises contacting a synthesis gas comprising a mixture of H<sub>2</sub> and CO with a hydrocarbon synthesis catalyst at synthesis reaction conditions sufficient for the H<sub>2</sub> and CO to react and form hydrocarbon products, wherein said catalyst comprises at least one catalytic metal component and at least one zeolite component formed by (i) adding a carbonate ion precipitant to an aqueous solution of at least one catalytic metal salt, to precipitate the catalytic metal as a first hydroxy metal carbonate and form a first slurry, followed by (ii) heating the slurry to remove CO<sub>2</sub> and form a CO<sub>2</sub>-reduced, second slurry containing a second hydroxy metal carbonate, (iii) compositing the second hydroxy metal precipitate with a zeolite component to form a catalyst precursor, (iv) drying the precursor to a moisture content of at least 6 wt. %, and (v) reducing the precursor with hydrogen to form the catalyst.

Typically, at least a portion of the synthesized hydrocarbons are upgraded by one or more upgrading operations which comprise fractionation and/or conversion in which at least a portion of the molecular structure of the hydrocarbons is changed. By hydrocarbons is meant to include oxygenated, olefinic and paraffinic hydrocarbons, with the paraffinic hydrocarbons preferably comprising C<sub>5+</sub> and more preferably C<sub>10+</sub> paraffins.

## DETAILED DESCRIPTION

- 5 -

As mentioned above, the exact procedure and conditions employed to form a hydroxylated or hydroxy metal carbonate precipitate, from an aqueous metal salt solution using a carbonate ion as a precipitant, has a strong influence on the structure of the precipitate and properties of the resulting catalyst. This is known and disclosed, for example, in an article by F. Cavani, et al., "Hydrotalcite-Type Anionic Clays: Preparation, Properties and Applications, on pages 173-215 of *Catalysis Today*, 11 (Elsevier, 1991). While not wishing to be held to any particular theory, it is believed that precipitating out the metal component(s) with a carbonate ion, produces a precipitate comprising a hydroxy metal carbonate having a hydrotalcite or hydrotalcite-like structure, according to Caviani, et al. The structure and carbon content of this hydroxy metal carbonate is believed to be altered both by driving CO<sub>2</sub> out of the resulting slurry and by the elevated temperature employed by the heating used to remove the CO<sub>2</sub> from the slurry, based on the performance characteristics and stability of the resulting catalyst. However, irrespective of any theory, it has been found that the properties of the final catalyst are significantly affected by these variables. The one or more catalytic metal component precursor salts will comprise one or more water-soluble inorganic or organic salts, such as a nitrate, acetate, formate and the like. Sulfur, phosphorus, halides and alkali metal-containing salts are to be avoided. The nitrates are often the salt of choice to the practitioner. The anion portion of the salt or salts must be decomposable at the reducing conditions used to form the catalyst from its precursor and leave no undesirable residues as a result of decomposition or adversely interfere with the reduction. In addition to containing one or metal salts of one or more catalytic metal components of the catalyst, the aqueous catalytic metal salt solution may also contain a metal salt of one or more promoter metals, such as magnesium (e.g., Mg(NO<sub>3</sub>)<sub>2</sub>\*6H<sub>2</sub>O), zirconium (e.g., ZrO(NO<sub>3</sub>)<sub>2</sub>\*2H<sub>2</sub>O) and the like. In this case the metals are coprecipitated and the resulting precipitate may comprise one or more bi- or multimetal hydroxy carbonates. Alternately, one or more promoter

- 6 -

metal oxides may be composited, along with the one or more zeolite components, with the catalytic metal precipitate remaining after CO<sub>2</sub> removal from the slurry. Thus, the aqueous catalytic metal component salt solution may contain salts of one or more catalytic metals, along with one or more salts of one or more catalytic promoters.

In the practice of the invention, the carbonate ion precipitant is added to the aqueous catalytic metal salt solution, under mixing conditions, to form the hydroxy metal carbonate precipitate. By mixing conditions is meant agitation or mixing sufficient to form an intimate mixture of the source of carbonate ion and salt solution, during the precipitation. The aqueous carbonate and/or bicarbonate salt solution may comprise more than one carbonate and/or bicarbonate salts, with the cation being one or more metals, preferably alkali metal, and/or ammonium ion, depending on the desired catalyst. While carbonate or bicarbonate salts may also be used, carbonates are preferred. The aqueous carbonate solution will typically comprise from 1 to 20 wt. % of one or more ammonium or alkali carbonates. It is important to the practice of the invention, that the sequence of adding the aqueous carbonate salt solution to the aqueous catalytic metal component salt solution to form the precipitate be followed. A catalyst of the invention will not be formed, if the catalytic metal salt solution is added to the carbonate solution.

In order to form a catalyst of the invention, after the hydroxy metal carbonate has been precipitated by the carbonate ion to form a first slurry, the resulting aqueous slurry containing the precipitate must be heated at an elevated temperature of preferably greater than 150°F, to drive out and remove CO<sub>2</sub>. The exact time and temperature may vary, along with the pressure, but it has been found satisfactory to heat the slurry at its boiling point. Heating is preferably maintained until CO<sub>2</sub> evolution ceases. The heating time at a given temperature

- 7 -

and pressure must be determined experimentally. As mentioned above, this alters the form of the precipitated hydroxy metal carbonate and results in a CO<sub>2</sub>-reduced, second slurry. It is this altered precipitate that is composited with the one or more zeolite components of the catalyst.

The one or more zeolites in particulate form may be composited with the precipitate resulting from the CO<sub>2</sub> removal by any well known methods. Thus, the precipitate may be separated from the slurry liquid by filtration or other separation means, to form a paste which is then intimately mixed and kneaded with the zeolite(s) and one or more other components, such as one or more promoter or support components, to form a catalyst precursor composite. More typically, at least one zeolite component of the catalyst, in particulate form, is composited with the precipitate, by contacting it, in particulate form, with the precipitate in the second slurry, under mixing conditions to form an intimate mixture of precipitate and zeolite, followed by filtration to form a paste. The paste is then extruded to the desired shape and size and dried. The drying is conducted at a temperature (e.g., 105-125°C) and for a time (e.g., 50-250 minutes) sufficient for the resulting catalyst precursor to have a moisture content of at least 6 wt. %. The precursor is then reduced, typically in flowing hydrogen or a hydrogen-containing reducing gas, at an elevated temperature sufficient to achieve reduction of the metal. It is preferred that the precursor contain at least 6 wt. % H<sub>2</sub>O and preferably no more than 15 wt. % H<sub>2</sub>O, prior to reduction, to form a more active catalyst. This is based on experimental results. In determining the residual moisture content of catalyst precursors made according to the process of the invention, a sample of washed and dried extrudate was placed in a drying oven in air, for varying times at 105-110°C to drive off the residual moisture, until there was no change in weight. This was taken as zero moisture content. Actual times varied from 65 to 170 minutes. The residual moisture content of the precursor extrudate was determined by the difference



- 8 -

between the constant weight, of which there was no further change in with increased drying time, and the weight of the precursor containing the residual moisture, prior to the further drying to constant weight. The moisture-containing precursor was then reduced with hydrogen as set forth below. The hydrogen-containing reducing gas may be all hydrogen, but will more typically comprise a mixture of hydrogen and any suitable inert gas. In this context, an inert gas is any gas which doesn't interfere with or affect the reduction, or alter the properties of the catalyst, and may comprise light hydrocarbons, argon, and the like. The reducing conditions include a pressure in the range of from 0.1 to 100 atm., preferably 1 to 50 atm. and more preferably from 1 to 10 atm. The reducing temperature will broadly range from 200 to 600°C, preferably from 300 to 450°C and more preferably from 325 to 450°C. The hydrogen reducing gas will comprise at least 10 vol. % of hydrogen.

In the practice of the invention, the one or more zeolite components of the catalyst catalyst will include shape selective molecular sieves which, when combined with at least one catalytic metal component, will be useful for the desired catalyst process for which the catalyst is intended. By zeolite is meant both natural and synthetic aluminosilicate molecular sieves, including but not limited to the A, X, Y, mordenite and ferrierite types, in both single and multivalent cation forms as well as the hydrogen forms and including dealuminized forms. The mole ratio of the silica to the alumina may range from 2 to 400 and the pore size may range from 4 to 15 . Such zeolites include, for example, in addition to ferrierite, and mordenite types, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-48, ZSM-22 also known as theta one or TON, Beta, MCM, L and the silicoaluminophosphates known as SAPO's. The zeolite component is preferably dehydrated prior to contacting the aqueous slurry. Further, the zeolite component may be composited with binder such as alumina, clay and the like, prior to contact with the catalytic metal-containing precipitate. Preferred

- 9 -

zeolites include at least one of a Y zeolite, an HY zeolite and a HZSM-5 zeolite. In some cases it is preferred that the zeolite be stabilized by being dealuminized, by any suitable method known to those skilled in the art.

The catalytic metal loading of the final catalyst will range, for cobalt as an example, from 5 to 70 wt. % and preferably from 20-40 wt. % of the total catalyst composition following reduction. Additional catalyst components may be added to or composited with the other catalytic components in conventional manners, either before the precipitation. Thus, and as mentioned above, one or more promoter metal salts of, for example, Zr, Mg, Th, Ti and the like may be coprecipitated with the one or more catalytic metal components. Alternately, one or more promoters and other components may be added to the precursor composite containing the second precipitate, subsequent to the precipitation or before or subsequent to, drying, but prior to reduction to form the catalyst. These may include, for example, one or more oxide promoters such as  $\text{ZrO}_2$ ,  $\text{ThO}_2$ ,  $\text{TiO}_2$  and like, typically in powdered form, as well as support components and binders. Such promoters will typically range from 0.1 to 20 wt. % of the catalyst composition, following reduction. While the catalytic metal and promoter metal components of the catalyst will depend on the process, suitable catalytic metals for a Fischer-Tropsch hydrocarbon synthesis process catalyst comprise, for example, one or more Group VIII metals such as Fe, Ni, Co and Ru and, in some cases, will comprise catalytically effective amounts of one or more Group VIII metals, such as Co, and one or more promoter metal components. Suitable promoter metals include Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La, composited with the zeolite component and one or more other suitable inorganic support materials, preferably which comprise one or more refractory metal oxides. The metal Groups referred to herein are those found in the Sargent-Welch Periodic Table of the Elements, © 1968. Titania is a useful component, particularly when employing a slurry hydrocarbon synthesis process

- 10 -

in which higher molecular weight, primarily paraffinic liquid hydrocarbon products are desired.

The hydrocarbons synthesized by a hydrocarbon synthesis process employing a catalyst prepared according to the practice of the invention are typically upgraded to more valuable products, by subjecting all or a portion of the hydrocarbon products produced in the synthesis reactor to one or more upgrading operations which include fractionation and/or one or more conversion operations. By conversion is meant one or more operations in which the molecular structure of at least a portion of the hydrocarbon is changed and includes both noncatalytic processing (e.g., steam cracking), and catalytic processing (e.g., catalytic cracking) in which a fraction is contacted with a suitable catalyst. If hydrogen is present as a reactant, such process steps are typically referred to as hydroconversion and include, for example, hydroisomerization, hydrocracking, hydrodewaxing, hydrotreating and the more severe hydrotreating referred to as hydrotreating, all conducted at conditions well known in the literature for hydroconversion of hydrocarbon feeds, including hydrocarbon feeds rich in paraffins. Illustrative, but nonlimiting examples of more valuable products formed by conversion include one or more of a synthetic crude oil, liquid fuel, olefins, solvents, lubricating, industrial or medicinal oil, waxy hydrocarbons, nitrogen and oxygen containing compounds, and the like. Liquid fuel includes one or more of motor gasoline, diesel fuel, jet fuel, and kerosene, while lubricating oil includes, for example, automotive, jet, turbine and metal working oils. Industrial oil includes well drilling fluids, agricultural oils, heat transfer fluids and the like.

With respect to the hydrocarbon synthesis, fixed bed, fluid bed and slurry hydrocarbon synthesis processes for forming hydrocarbons from a synthesis gas comprising a mixture of  $H_2$  and CO are well known and documented in the

- 11 -

literature. In all of these processes, the synthesis gas is reacted in the presence of a suitable Fischer-Tropsch type of hydrocarbon synthesis catalyst, at reaction conditions effective to form hydrocarbons. Except for a fluidized bed process in which the synthesis hydrocarbons are all gaseous at the reaction conditions, some of these synthesized hydrocarbons will be liquid, some solid (e.g., wax) and some gas at standard room temperature conditions of temperature and pressure of 25°C and one atmosphere, particularly if a catalyst having a catalytic cobalt component is used. Slurry processes are often preferred because of their superior heat (and mass) transfer characteristics for the strongly exothermic synthesis reaction and because they are able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst. In a slurry HCS process a synthesis gas comprising a mixture of H<sub>2</sub> and CO is bubbled up as a third phase through a slurry in a reactor which comprises a particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid at the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. The stoichiometric mole ratio for a Fischer-Tropsch hydrocarbon synthesis reaction is 2.0, but in the practice of the present invention it may be increased to obtain the amount of hydrogen desired from the synthesis gas for other than the HCS reaction. In a slurry process the mole ratio of the H<sub>2</sub> to CO is typically about 2.1/1. Slurry process conditions vary somewhat depending on the catalyst and desired products. Typical conditions effective to form hydrocarbons comprising mostly C<sub>5+</sub> paraffins, (e.g., C<sub>5+</sub>-C<sub>200</sub>) and preferably C<sub>10+</sub> paraffins, in a slurry HCS process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from about 320-600°F, 80-600 psi and 100-40,000 V/hr/V,

- 12 -

expressed as standard volumes of the gaseous CO and H<sub>2</sub> mixture (0°C, 1 atm) per hour per volume of catalyst, respectively.

The invention will be further understood with reference to the Examples below.

## EXAMPLES

In preparing the hydrocarbon synthesis catalysts of the invention, air-dried zeolites, without a binder, were dehydrated in an inert gas flow for 4 hr. at 480-500°C. After cooling down to room temperature in a dry box, they were introduced as a powder under intensive stirring into a solution of cobalt nitrate or cobalt and magnesium nitrates, to which a precipitant solution of either sodium carbonate or ammonium carbonate had previously been added, with the solution then heated at its boiling point until CO<sub>2</sub> evolution ceased. The metal precipitate comprises one or more hydroxy carbonates, the structure of which is changed by boiling until the cessation of CO<sub>2</sub> evolution. This was followed by filtering the resulting precipitate and washing the resulting paste with hot water to remove nitrate ions, followed by extruding and drying in air at 105-120°C for from 65-170 minutes to form a catalyst precursor, which was then reduced in hydrogen at 380-400°C to form the catalyst. Preferably, the duration and the temperature at which the drying is conducted is chosen to achieve a satisfactory residual moisture content in the precursor prior to the reduction, as determined by the color of the precursor. For example, it has been found that Co-Mg-containing catalyst precursors with too low of a moisture content (e.g., less than about 6 wt. %) had a grey color as opposed to a violet color exhibited by precursors with a higher moisture content. This color change is indicative of a change in precursor structure, when too much moisture is removed from the precursor prior to

- 13 -

reduction in hydrogen and is reflected in a catalyst with less CO conversion and C<sub>5+</sub> hydrocarbon yield.

When used for hydrocarbon synthesis, at a synthesis gas pressure slightly above atmospheric, there was no decrease in activity over the 60-80 hr. runs in the laboratory fixed bed reactor. In preparing the catalysts, various single- and multivalent cation forms (Na, Ca, NH<sub>4</sub>, H<sub>2</sub>, etc.) of the zeolites are used as the supports or the zeolite component of the catalysts. Zeolites having a wide range of pore sizes were found to be effective and included, for example, X zeolites having a pore size of 8-9 , Y zeolites having a pore size of 7 , as well as the decationated form of Y zeolites and the hydrogen form of synthetic mordenite. The various zeolites were prepared from original sodium-containing zeolites, by ion exchange with 2-10 wt. % aqueous solutions of either chlorides or nitrates of the corresponding metals, in the case of cation forms, or solutions of either ammonium chloride or ammonium nitrate in the case of the hydrogen forms of the Y and mordenite zeolites. The latter may also be produced by direct treatment of Na-mordenite with a 2N solution of HCl at room or elevated (80-90°C) temperature. Further, A zeolites having pores of 4-5 are also effective.

#### Example 1

A precipitant solution of 16 g of sodium carbonate dissolved in 80 g of water was added to a solution of 25 g of cobalt nitrate dissolved in 100 g of water, and the combined solutions heated to boiling. Boiling was continued until CO<sub>2</sub> evolution ceased. The resulting suspension was cooled and 10 g of powdered, dehydrated NaX zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 2.5) added to it to form a slurry. The zeolite had been dehydrated by being heated for 5 hours at 500°C, under dry, flowing N<sub>2</sub> and kept dry until it was added to the suspension. The

- 14 -

slurry was stirred for 10 min. at room temperature and filtered. The filter cake was washed with hot water to remove nitrate ions, formed into a paste and extruded into 2x3-4 mm cylinders, which were dried in air at 110-120°C. The extrudates had a composition of 100Co:200NaX.

The dry extrudates were then loaded into a fixed bed laboratory reactor and reduced under flowing H<sub>2</sub> at 350-400°C (GHSV of 100 hr<sup>-1</sup>) for 5 hr. A synthesis gas comprising a mixture of H<sub>2</sub> and CO having an H<sub>2</sub>:CO mole ratio of 2:1, at a space velocity of 90 hr<sup>-1</sup>, was passed through the catalyst bed at 190°C. The pressure was slightly above atmospheric. The gas contraction was 67.6 vol. % and this was also the amount of CO conversion. The synthesized hydrocarbons were successively passed through a cold water trap (17-22°C), followed by a dry ice trap. The C<sub>5+</sub> liquid yield was 123 g/m<sup>3</sup> (STP), with a gasoline fraction to heavier oil product liquid weight ratio of 1.4:1. By gasoline fraction is meant the liquid condensate in the dry ice trap, while the heavier oil was the liquid condensate in the cold water trap, which preceded the dry ice trap.

Thus, this catalyst exhibited excellent selectivity for gasoline production at a relatively low reaction temperature, with good CO conversion.

### Example 2

A hydrogen substituted Y zeolite was prepared by ion exchange according to well known procedures as described, for example, in US patents 3,287,282 and 3,503,901. A 0.01 N aqueous solution of NH<sub>4</sub>Cl was prepared. Three mole equivalents of this solution was added to the sodium form of the Y zeolite, so that there was three mole equivalents of NH<sub>4</sub><sup>+</sup> ion present, for each mole equivalent of Na<sup>+</sup> ion in the zeolite, during the ion exchange reaction. The suspension was stirred and heated to 80°C. It was held at 80°C for 2 hours.

- 15 -

Then the solution was decanted and the zeolite was dried in air at 100-120°C for 2 hours. The zeolite was then placed in a quartz reactor and calcined in flowing N<sub>2</sub> or He at 400°C for 4 hours. Then the zeolite was cooled and removed from the reactor. The extent of ion exchange (H<sup>+</sup> for Na<sup>+</sup>) was 70%. The resulting HNaY zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.4:1, 70 % Na<sup>+</sup> exchange) was stored under nitrogen in a dry box until use.

In this experiment, a precipitant solution of 16 g of sodium carbonate dissolved in 80 g of water, was added to a solution of 25 g of cobalt nitrate and 3.2 g of magnesium nitrate dissolved in 100 g of water, and the combined solutions heated to boiling. Boiling continued until CO<sub>2</sub> evolution ceased. The resulting suspension was cooled and 10 g of the powdered, dehydrated HNaY zeolite added to it to form a slurry. The slurry was stirred for 10 min. at room temperature and filtered. The filter cake was washed with hot water to remove nitrate ions, formed into a paste and extruded into 2x3-4 mm cylinders, which were dried in air at 110-120°C. The extrudates had a composition of 100Co:10MgO:200HNaY.

The dry extrudates were then loaded into a fixed bed laboratory reactor and reduced under flowing H<sub>2</sub> at 350-400°C (GHSV of 100 hr<sup>-1</sup>) for 5 hr. A synthesis gas comprising a mixture of H<sub>2</sub> and CO having an H<sub>2</sub>:CO mole ratio of 2:1, at a space velocity of 103 hr<sup>-1</sup>, was passed through the catalyst bed at 180°C and a pressure slightly above atmospheric. The gas contraction was 83.5 vol. % and this was also the amount of CO conversion. The C<sub>5+</sub> liquid yield was 145.5 g/m<sup>3</sup> (STP).



- 16 -

Thus, this catalyst exhibited excellent selectivity for C<sub>5+</sub> liquid production, at a relatively low reaction temperature, with even greater CO conversion than in Example 1.

### Example 3

The sodium form of a Y zeolite was mixed with a 10-fold mole excess of a 10 wt % aqueous CaCl<sub>2</sub> solution, for 4 hours at 80°C. Then the solution was decanted and the zeolite was dried in air at 100-120°C for 2 hours. The zeolite was then placed in a quartz reactor and calcined in flowing N<sub>2</sub> or He at 400°C for 4 hours. Then the zeolite was cooled and removed from the reactor. The extent of ion exchange (Ca<sup>+2</sup> for Na<sup>+</sup>) was 67% and the composition of the resulting zeolite was SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.4:1.

A catalyst having a composition of 100Co:10MgO:200CaNaY (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.4, 67 % total Ca<sup>+</sup>, Na<sup>+</sup> exchange) was prepared, extruded and reduced using the same procedure used in Example 2, and then loaded into the fixed bed laboratory reactor. The CaNaY zeolite added to the combined solutions after CO<sub>2</sub> removal, was dehydrated as in Example 2. The same 2:1 H<sub>2</sub> to CO mole ratio synthesis gas composition was again used. At the same reaction conditions of a temperature of 180°C, a pressure slightly above atmospheric and a GHSV of 100 hr<sup>-1</sup>, the gas contraction was 84 %, which meant a CO conversion of 84 %, and the C<sub>5+</sub> yield of synthesized hydrocarbons was 142 g/cm<sup>3</sup> (STP).

### Example 4

- 17 -

The sodium form of mordenite zeolite was mixed with a 3-fold mole excess of an aqueous, 2N HCl solution at 95°C. Then the solution was decanted and the zeolite was dried in air at 100-120°C for 2 hours. The zeolite was then placed in a quartz reactor and calcined in flowing N<sub>2</sub> or He at 400°C for 4 hours. Then the zeolite was cooled and removed from the reactor. The extent of ion exchange (H<sup>+</sup> for Na<sup>+</sup>) was 100% and the SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> mole ratio of the resulting H- mordenite zeolite was 10.5.

A catalyst using this H-mordenite (HM) type of zeolite was prepared using the procedure of Example 2 and had a composition of 100Co:10MgO:200HM (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 10.5, 100 % exchange). The HM had been dehydrated prior to being added to the combined solutions after CO<sub>2</sub> removal. Except for a temperature of 191°C, the other reaction conditions were the same as in Example 2. The gas contraction was 86.6 vol. % and the liquid hydrocarbon yield was 110 g/m<sup>3</sup> (STP).

It is understood that various other embodiments and modifications in the practice of the invention will be apparent to, and can be readily made by, those skilled in the art without departing from the scope and spirit of the invention described above. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the exact description set forth above, but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all the features and embodiments which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

- 18 -

CLAIMS:

1. A process for forming a catalyst comprising at least one catalytic metal component, optionally one or more promoter components and at least one zeolite component, comprises:

(i) adding a carbonate ion precipitant, under mixing conditions, to an aqueous solution of one or catalytic metal salts, to form a slurry comprising a precipitate comprising a first hydroxy metal carbonate of said one or more catalytic metal components;

(ii) heating said slurry to remove CO<sub>2</sub> to change said first hydroxy metal carbonate to a second hydroxy metal carbonate and form a CO<sub>2</sub>-reduced, second slurry containing said second hydroxy metal carbonate precipitate;

(iii) compositing said second hydroxy metal carbonate precipitate said CO<sub>2</sub>-reduced slurry with said at least one zeolite component to form a composite of said precipitate and zeolite;

(iv) drying said composite to form a catalyst precursor containing between 6 to 15 wt. % residual moisture, and

(v) reducing said precursor with hydrogen to form said catalyst.

2. A process according to claim 1 wherein an aqueous solution of one or more carbonate or bicarbonate salts is added to said catalytic metal salt solution, to provide said carbonate ion precipitant.

- 19 -

3. A process according to claim 2 wherein said slurry is heated until said CO<sub>2</sub> evolution ceases.

4. A process according to claim 1 wherein said zeolite component is dehydrated prior to being contacted with said CO<sub>2</sub>-reduced slurry.

5. A process according to claim 1 wherein said catalytic metal comprises one or more metals of Group VIII of the Periodic Table of the Elements.

6. A process according to claim 5 wherein said zeolite comprises at least one of a Y zeolite, an HY zeolite and an HZSM-5 zeolite.

7. A process according to claim 5 wherein said catalyst contains one or more promoter metal components.

8. A process according to claim 5 wherein said catalytic metal comprises cobalt.

9. A process according to claim 7 wherein said promoter metal comprises at least one of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La.

10. A process according to claim 1 wherein said zeolite comprises a stabilized zeolite.

11. A process according to claim 9 wherein said promoter metal is selected from the group consisting essentially of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La, and mixture thereof.

- 20 -

12. A hydrocarbon synthesis process comprises contacting a synthesis gas comprising a mixture of  $H_2$  and CO with a hydrocarbon synthesis catalyst at synthesis reaction conditions sufficient for the  $H_2$  and CO to react and form hydrocarbon products, wherein said catalyst comprises at least one catalytic metal component and at least one zeolite component and has been formed by a process which comprises the steps of:

(i) adding a carbonate ion precipitant, under mixing conditions, to an aqueous solution of one or catalytic metal salts, to form a slurry comprising a precipitate comprising a first hydroxy metal carbonate of said one or more catalytic metal components;

(ii) heating said slurry to remove  $CO_2$  to change said first hydroxy metal carbonate to a second hydroxy metal carbonate and form a  $CO_2$ -reduced, second slurry containing said second hydroxy metal carbonate precipitate;

(iii) compositing said second hydroxy metal carbonate precipitate said  $CO_2$ -reduced slurry with said at least one zeolite component to form a composite of said precipitate and zeolite;

(iv) drying said composite to a moisture content of 6 and 15 wt. % to form a catalyst precursor, and

(v) reducing said precursor with hydrogen to form said catalyst.

13. A process according to claim 12 wherein an aqueous solution of one or carbonate or bicarbonate salts is added to said catalytic metal salt solution to provide said carbonate ion precipitant.

- 21 -

14. A process according to claim 12 wherein said slurry is heated until said CO<sub>2</sub> evolution ceases.

15. A process according to claim 12 wherein said catalytic metal comprises one or more metals of Group VIII of the Periodic Table of the Elements.

16. A process according to claim 12 wherein said zeolite comprises at least one of a Y zeolite, an HY zeolite and an HZSM-5 zeolite.

17. A process according to claim 15 wherein said catalyst contains one or more promoter metal components.

18. A process according to claim 15 wherein said catalytic metal comprises cobalt.

19. A process according to claim 17 wherein said promoter metal comprises at least one of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La.

20. A process according to claim 12 wherein said zeolite comprises a stabilized zeolite.

21. A process according to claim 19 wherein said promoter metal is selected from the group consisting essentially of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La, and mixture thereof.

22. A process according to claim 12 wherein at least a portion of said synthesized hydrocarbons are upgraded by one or more upgrading operations,

- 22 -

including fractionation or conversion to alter at least a portion of the molecular structure of the hydrocarbon.

23. A process according to claim 15 wherein at least a portion of said synthesized hydrocarbons are upgraded by one or more upgrading operations, including fractionation or conversion to alter at least a portion of the molecular structure of the hydrocarbon.

# INTERNATIONAL SEARCH REPORT

Internati Application No  
PCT/US 00/27715

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01J37/03 B01J37/08 B01J29/06 C07C1/04

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)  
IPC 7 B01J C07C

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 practical, search terms used)  
EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 659 743 A (RAO V UDAYA S ET AL) 21 April 1987 (1987-04-21) column 4, line 22 -column 4, line 64 ----	1-23
X	US 4 849 571 A (GAFFNEY ANNE M) 18 July 1989 (1989-07-18) example 11 ----	1-23
A	US 2 850 515 A (RIBLETT E.W. ET AL) 2 September 1958 (1958-09-02) cited in the application ----	
A	US 4 086 262 A (SILVESTRI ANTHONY J ET AL) 25 April 1978 (1978-04-25) cited in the application -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### ° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*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

- \*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
- \*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

31 January 2001

Date of mailing of the international search report

(12 .02 .01)

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 00/27715

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: **Claims 1-4, 12-14**  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
**see FURTHER INFORMATION sheet PCT/ISA/210**
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: Claims 1-4, 12-14

Present claims 1-4 and 12-14 relate to an extremely large number of possible catalysts to be prepared.

Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the catalysts to be prepared.

In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the preparation of catalysts comprising at least one catalytic metal of Group VIII

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/27715

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4659743 A	21-04-1987	AU 575016 B	21-07-1988
		AU 8892982 A	14-04-1983
		CA 1177464 A	06-11-1984
		JP 58071987 A	28-04-1983
US 4849571 A	18-07-1989	NONE	
US 2850515 A	02-09-1958	NONE	
US 4086262 A	25-04-1978	NONE	