(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: HYDROCARBON SYNTHESIS CATALYST ENHANCEMENT WITH HYDROGEN AND AMMONIA

(57) Abstract: Hydrocarbon synthesis catalysts are enhanced to improved performance, by contacting the catalyst with a reducing gas comprising a mixture of hydrogen and ammonia, at elevated temperature and pressure effective for conventional synthesis catalyst reduction. It is preferred that a portion of the total reduction be achieved with a reducing gas comprising ammonia and hydrogen and the balance with a hydrogen reducing gas without ammonia.

- 1 -

HYDROCARBON SYNTHESIS CATALYST ENHANCEMENT WITH HYDROGEN AND AMMONIA

BACKGROUND OF THE DISCLOSURE

Field of the Invention

The invention relates to enhancing a hydrocarbon synthesis catalyst with hydrogen and ammonia. More particularly, the invention relates to improving the performance of a hydrocarbon synthesis catalyst, including a Fischer-Tropsch type of hydrocarbon synthesis catalyst, by contacting the catalyst with a reducing gas comprising a mixture of hydrogen and ammonia, at catalyst reduction conditions, and to a hydrocarbon synthesis process using the enhanced catalyst.

Background of the Disclosure

The synthesis of hydrocarbons, including oxygenated hydrocarbons such as methanol, from a synthesis gas comprising a mixture of H_2 and CO is well known. The synthesis gas feed is contacted with a Fischer-Tropsch catalyst at conditions effective for the H_2 and CO in the feed gas to react and form hydrocarbons. The synthesis is known as a Fischer-Tropsch hydrocarbon synthesis. Depending on the catalyst and conditions, the hydrocarbons may range from oxygenated compounds such as methanol and higher molecular weight alcohols, to high molecular weight paraffins which are waxy solids at room temperature. The process also makes, in lesser amounts, alkenes, aromatics, organic acids, ketones, aldehydes and esters. The synthesis is conducted in a fixed or fluidized catalyst bed reactor or in a liquid phase slurry

reactor. Hydrocarbon synthesis catalysts are also well known and typically include a composite of at least one iron group catalytic metal component supported on, or composited with, with at least one inorganic refractory metal oxide support material, such as alumina, amorphous, silica-alumina, zeolites and the like. Various catalyst preparation methods have been used to form hydrocarbon synthesis catalysts, including impregnation, incipient wetness, compositing, ion exchange and other known techniques, to form a catalyst precursor. The precursor must be activated to form the catalyst. Typical activation methods include oxidation or calcination, followed by reduction in flowing hydrogen, multiple oxidation-reduction cycles and also reduction without prior oxidation. Examples of catalyst preparation and activation methods for Fischer-Tropsch hydrocarbon synthesis catalysts are disclosed in, for example, US patents US 4,086,262 ; 4,492,774 and 5,545,674.

SUMMARY OF THE INVENTION

The invention relates to enhancing or improving the performance of an active hydrocarbon synthesis catalyst, including a Fischer-Tropsch type of hydrocarbon synthesis catalyst, by contacting the catalyst with a reducing gas comprising a mixture of hydrogen and ammonia, at conventional catalyst reduction conditions effective to form a active catalyst, and to a hydrocarbon synthesis process using the enhanced catalyst. By catalyst is meant an active hydrocarbon synthesis catalyst wherein at least a portion, and preferably only a portion, of the one or more catalytic metals (e.g., Co, Fe, Ni) is in the reduced or catalytically active metal form, as a consequence of reduction achieved by contacting the catalyst precursor in a hydrogen reducing gas without ammonia, at conventional hydrogen reducing conditions. Thus, while the catalyst may be completely reduced and fully active prior to contact with the hydrogen and

- 3 -

ammonia mixture in the practice of the invention, it is preferred that it be partially reduced in hydrogen without ammonia and partially reduced in a reducing gas comprising hydrogen and ammonia, to achieve complete reduction and activation. It has been found that contacting the catalyst with a reducing gas comprising a mixture of hydrogen and ammonia enhances the hydrocarbon synthesis properties of the resulting active catalyst, with respect to at least one of; increased C_{5+} selectivity, increased alpha (Schultz-Flory alpha) of the synthesis reaction, and a reduction in methane make. These benefits are unexpected, in view of the fact that ammonia is a well known hydrocarbon synthesis catalyst poison. Thus, by enhanced catalyst, in the context of the invention, is meant that at least one, preferably at least two, and more preferably all three of the following are achieved during hydrocarbon synthesis: (i) the C_{5+} selectivity of the catalyst is greater than it otherwise would be if the catalyst had not been contacted with a reducing gas comprising a mixture of hydrogen and ammonia; (ii) the alpha of the synthesis reaction is greater than it would otherwise be if the catalyst had not been contacted with a reducing gas comprising a mixture of hydrogen and ammonia, and (iii) the methane make is reduced to a level lower than it would otherwise be if the catalyst had not been contacted with a reducing gas comprising a mixture of hydrogen and ammonia.

The catalyst precursor may or may not be calcined prior to activation by reduction. Either or both the hydrogen reducing gas, and the reducing gas comprising the mixture of hydrogen and ammonia, may or may not contain one or more diluent gasses which do not adversely effect or interfere with the reduction and concomitant activation of the catalyst. Such gasses include methane, argon and the like. The amount of ammonia present in the hydrogen reducing gas will broadly range from 0.01 to 15 mole %, preferably 0.01 to 10 mole %, more preferably from 0.1 to 10 mole % and still more preferably from 0.5 to 7 mole %, based on the total gas composition. The hydrogen to ammonia

- 4 -

mole ratio in the gas will range from 1000:1 to 5:1 and preferably from 200:1 to 10:1.

In one embodiment the invention is a process which comprises enhancing a Fischer-Tropsch type of hydrocarbon synthesis catalyst, comprising at least one catalytic metal component, and preferably at least one catalytic metal component and a metal oxide support type of component, by contacting the catalyst with a reducing gas comprising a mixture of hydrogen and ammonia, at catalyst reduction conditions effective to reduce the one or more catalytic metal components to the reduced, catalytically active metal form, and preferably wherein a portion of the one or more catalytic metal components is reduced to the catalytically active metal form as a result of the contacting. In another embodiment, the invention comprises a process for synthesizing hydrocarbons from a synthesis gas which comprises a mixture of H_2 and CO, wherein the synthesis gas is contacted with an enhanced Fischer-Tropsch type of hydrocarbon synthesis catalyst, at reaction conditions effective for the H_2 and CO in the gas to react and form hydrocarbons, wherein the enhanced catalyst comprises a composite of at least one catalytic metal component and metal oxide support component, and has been enhanced by contacting the catalystwith a reducing gas comprising a mixture of hydrogen and ammonia, at catalyst reduction conditions effective to reduce the one or more catalytic metal components to the reduced, catalytically active metal form, and preferably wherein a portion of the one or more catalytic metal components is reduced to the catalytically active metal form as a result of the contacting. In a still further embodiment, at least a portion of the synthesized hydrocarbons are liquid at the reaction conditions. By conventional catalyst reduction conditions is meant conditions of temperature, pressure, hydrogen partial pressure and the space velocity of a conventional hydrogen reducing gas, sufficient to reduce the one or

more catalytic metal components of the precursor to the metal and form an active catalyst.

DETAILED DESCRIPTION

Hydrocarbon synthesis catalysts are well known and a typical Fischer-Tropsch hydrocarbon synthesis catalyst will comprise, for example, catalytically effective amounts of one or more Group VIII metal catalytic components such as Fe, Ni, Co and Ru. Preferably the catalyst comprises a supported catalyst, wherein the one or more support components of the catalyst will comprise an inorganic refractory metal oxide. The metal oxide support component is preferably one which is difficult to reduce, such an oxide of one or more metals of Groups III, IV, V, VI, and VII. The metal Groups referred to herein are those found in the Sargent-Welch Periodic Table of the Elements, © 1968. Typical support components include one or more of alumina, silica, and amorphous and crystalline aluminosilicates, such as zeolites. Particularly preferred support components are the Group IVB metal oxides, especially those having a surface area of 100 m^2/g or less and even 70 m^2/g or less. These support components may, in turn, be supported on one or more support materials. Titania, and particularly rutile titania, is a preferred support component, especially when the catalyst contains a cobalt catalytic component. Titania is a useful component, particularly when employing a slurry hydrocarbon synthesis process, in which higher molecular weight, primarily paraffinic liquid hydrocarbon products are desired. In some cases in which the catalyst comprises catalytically effective amounts of Co, it will also comprise one or more components or compounds of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La, some of which are effective as promoters. A combination of Co and Ru is often preferred. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be

found, for example, in U.S. patents 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674.

The catalysts are prepared by any convenient and known method, such as impregnation, incipient wetness, ion exchange, kneading, precipitation or coprecipitation, melt deposition or any other compositing techniques to form the catalyst precursor. The catalytic metal component is typically applied as a solution of a compound which decomposes during the subsequent calcination and/or reduction. For example, a cobalt component is typically applied as a nitrate salt. It is not uncommon to calcine the precursor after each application of reducible catalytic metal compound, to achieve better catalytic metal dispersion. After forming and extruding the precursor composite, it is typically pilled and dried. The precursor is then reduced or calcined and reduced, to form the catalyst. The reduction is achieved by contacting the precursor with flowing hydrogen or a hydrogen reducing gas, at conditions effective to reduce the catalytically active metal component (e.g., cobalt) to the metal form. A common method is known as the R-O-R method, in which the precursor is reduced in hydrogen, then calcined, followed by reducing again. As mentioned above, the reducing hydrogen gas can be neat (all hydrogen), or mixed with one or more diluent gasses (e.g., methane, argon) which are inert towards the reduction. In the practice of the invention, the R-O-R method may also be used and a conventional hydrogen reducing gas used for the first and at least a portion of the second reduction, and preferably with a portion of the final reduction achieved by a reducing gas comprising a mixture of hydrogen and ammonia. Typical reducing conditions effective for forming the catalyst comprising the reduced metal component on the support from the precursor, range from ½ to 24 hours, 200-500°C, 1-100 bar, and a GHSV of 50-10000. The actual conditions will depend on the hydrogen concentration in the reducing gas, as well as the metal to be reduced and its precursor form (e.g., salt or oxide). In the catalyst

- 7 -

enhancing process of the invention, the at least partially reduced and active catalyst is contacted with a mixture of a hydrogen reducing gas and ammonia, at typical reducing conditions, as set forth above, similar to those used for normal reduction and concomitant activation. The catalyst enhancement may be conducted according to the process of the invention, either prior to loading it into the hydrocarbon synthesis reactor or in-situ in the hydrocarbon synthesis reactor.

The enhanced catalyst may be used in either a fixed bed, fluid bed or slurry hydrocarbon synthesis processes, for forming hydrocarbons from a synthesis gas comprising a mixture of H_2 and CO. These processes are well known and documented in the literature. In all of these processes, the synthesis gas is contacted with a suitable Fischer-Tropsch type of hydrocarbon synthesis catalyst, at reaction conditions effective for the H_2 and CO in the gas to react and form hydrocarbons. Depending on the process, the catalyst and synthesis reaction variables, some of these hydrocarbons will be liquid, some solid (e.g., wax) and some gas at standard room temperature conditions of temperature and pressure of $25^{\circ}C$ and one atmosphere, particularly if a catalyst having a catalytic cobalt component is used. In a fluidized bed hydrocarbon synthesis process, all of the products are vapor or gas at the reaction conditions. In fixed bed and slurry processes, the reaction products will comprise hydrocarbons which are both liquid and vapor at the reaction conditions. Slurry hydrocarbon synthesis processes are sometimes 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 hydrocarbon synthesis process, a synthesis gas comprising a mixture of H_2 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

- 8 -

liquid at the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide in the synthesis gas 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 it can be increased to obtain the amount of hydrogen desired from the synthesis gas for other than the hydrocarbon synthesis reaction. In a slurry hydrocarbon synthesis process, the mole ratio of the H_2 to CO is typically about 2.1/1. Reaction conditions effective for the various hydrocarbon synthesis processes will vary somewhat, depending on the type of process, catalyst composition and desired products. Typical conditions effective to form hydrocarbons comprising mostly C_{5+} paraffins, (e.g., C_{5+}-C_{200}) and preferably C_{10+} paraffins, in a slurry 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, expressed as standard volumes of the gaseous CO and H_2 mixture (0°C, 1 atm) per hour per volume of catalyst, respectively. These conditions nominally apply to the other processes as well.

Hydrocarbons produced by a hydrocarbon synthesis process according to the practice of the invention are typically upgraded to more valuable products, by subjecting all or a portion of the C_{5+} hydrocarbons to fractionation and/or conversion. 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, hydrorefining and the more severe hydrorefining 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.

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

EXAMPLES

Example 1 (Silica support)

A commercially available silica gel known as KCKG #4 (manufactured by Salavat Catalyst Factory of the Salavat Petrochemical Complex, Salavant, Russia), 2-4 mm diameter, was ground and sieved to obtain a 0.106-0.250 mm size fraction. This material was then calcined in flowing air at 450°C for 5 hours, to form the support for the catalysts prepared below.

Example 2 (Catalyst A precursor)

A solution of 5.18 gm of $Co(NO_3)_2*6H_2O$ in 15 ml of distilled water was prepared. This solution was added to 21 ml (8.38 gm) of the calcined silica support from Example 1, with stirring, to form a catalyst precursor. Then the

- 10 -

catalyst precursor was dried on a steam bath. At this stage, the catalyst precursor contained nominally 11 wt % cobalt and is the catalyst A precursor.

Example 3 (Catalyst B precursor)

An aqueous solution of 4.9 gm of $ZrO(NO_3)_2*2H_2O$ was added to 33.2 gm of the calcined silica support of Example 1, in a volume of water sufficient to fully wet the silica, which was then dried over a steam bath, followed by calcining in flowing air for 1 hour at 450°C, to form a first composite. Then a solution of 75 gm of $Co(NO_3)_2*6H_2O$ in 30 ml of water was added to the composite which soaked for 2 hours at room temperature. The excess solution was decanted off and saved. The resulting second composite was dried on a steam bath and then calcined in flowing air for 2 hours at 450°C. After cooling, the saved excess solution was added to the second composite. The steps of soaking, decanting, drying, and calcining were repeated until all of the $Co(NO_3)_2*6H_2O$ solution was impregnated onto the composite to form the final catalyst precursor, which is the catalyst B precursor. The so-formed catalyst B precursor contained 27 wt. % cobalt and 4.1 wt. % zirconium oxide.

Example 4 (Catalyst B reduction in H_2)

The catalyst B precursor of Example 3 (20 ml) was mixed with 80 ml of 1-3 mm quartz particles and the mixture placed into a 25 mm ID quartz reactor. The catalyst/quartz mixture was held in place with glass wool at the bottom of the reactor and a layer consisting of 10 ml of the 1-3 mm quartz particles on top of the catalyst/quartz mixture. Hydrogen was then passed through the reactor at room temperature and atmospheric pressure at a gas hourly space velocity (GHSV) of 100 hr^{-1} for 15 minutes. Prior to entering the reactor, the hydrogen was passed through a column of KOH pellets (pellet diameter nominally 3-5

mm) for removal of impurities. The reactor temperature was increased to 450°C over 40-45 minutes. This condition was held for 5 hours. Then the reactor was allowed to cool to room temperature in flowing hydrogen. After the reactor had cooled, the hydrogen flow was replaced with a flow of 2:1 H_2:CO synthesis gas at 100 hr^{-1} GHSV, for 15 minutes at atmospheric pressure. As with the hydrogen, the synthesis gas was passed through a column of KOH pellets for removal of impurities. Then valves were closed at the inlet and outlet of the reactor, storing the catalyst under the synthesis gas.

Example 5 (Catalyst B reduction in H_2 and then NH_3/H_2)

A 20 ml sample of the catalyst B precursor of Example 3 was mixed with 80 ml of 1-3 mm quartz particles and the mixture placed into a 25 mm ID quartz reactor. The catalyst/quartz mixture was held in place with glass wool at the bottom of the reactor and a layer consisting of 10 ml of the 1-3 mm quartz particles on top of the catalyst/quartz mixture. Hydrogen was then passed through the reactor at room temperature and atmospheric pressure at a gas hourly space velocity (GHSV) of 100 hr^{-1} for 15 minutes. Prior to entering the reactor, the hydrogen was passed through a column of KOH pellets (pellet diameter nominally 3-5 mm) for removal of impurities and through a 3-necked flask containing NaOH pellets. The center neck of the 3-necked flask was equipped with a syringe for addition of 29 wt % NH_3/ 71 wt % H_2O solution. The NaOH in the 3-necked flask served to absorb the water from the NH_3/H_2O solution, liberating the NH_3 vapor, which was then swept out of the flask and into the reactor. The reactor temperature was increased to 400°C over 40-45 minutes. In preparing the catalysts, the procedure used in Example 4 (in which the reactor temperature was increased from room temperature to 450°C over 40-45 minutes and held at 450°C for 5 hours) was used until the reactor reached the 450°C temperature. This was followed by 5 hours of reduction (i) with H_2 only for the

- 12 -

first sample, (ii) with H_2 followed a mixture of H_2 and NH_3 for the next four samples and (iii) with a mixture of H_2 and NH_3 only for the fifth sample, as shown in Table 2 below. Ammonia addition into the H_2 gas to provide the H_2/NH_3 reducing gas mixture, was achieved by a continuous drop-wise addition of the 29 wt % NH_3/ 71 wt % H_2O solution from the syringe. The nominal concentration of NH_3 in the reducing gas during the NH_3/H_2O solution addition was 5 mole %. Irrespective of whether the reduction was achieved with (i) all H_2, (ii) H_2 followed by the H_2/NH_3, or (iii) all H_2/NH_3, the total reduction time was 5 hours, as shown in Table 2. Following reduction, the reactor was allowed to cool to room temperature in flowing hydrogen. After the reactor had cooled, the hydrogen flow was replaced with a flow of 2:1 H_2:CO synthesis gas at 100 hr^{-1} GHSV for 15 minutes at atmospheric pressure. As with the hydrogen, the synthesis gas was passed through a column of KOH pellets, for removal of impurities. Then valves were closed at the inlet and outlet of the reactor, storing the catalyst under the synthesis gas.

Example 6 (Catalyst A reduction with NH_3/H_2)

A 20 ml sample of the catalyst A precursor of Example 2 was mixed with 80 ml of 1-3 mm quartz particles and the mixture placed into a 25 mm ID quartz reactor. The catalyst/quartz mixture was held in place with glass wool at the bottom of the reactor and a layer consisting of 10 ml of the 1-3 mm quartz particles on top of the catalyst/quartz mixture. Hydrogen was then passed through the reactor at room temperature and atmospheric pressure at a gas hourly space velocity (GHSV) of 3000 hr^{-1} for 15 minutes. Prior to entering the reactor, the hydrogen was passed through a column of KOH pellets (pellet diameter nominally 3-5 mm) for removal of impurities and through a 3-necked flask containing NaOH pellets. The center neck of the 3-necked flask was equipped with a syringe for addition of 29 wt % NH_3/ 71 wt % H_2O solution. The NaOH

in the 3-necked flask served to absorb the water from the NH_3/H_2O solution,

liberating the NH_3 vapor, which was then swept out of the flask to the reactor.

The reactor temperature was increased to 400°C over 40-45 minutes. After

reaching 400°C, drop-wise addition of the 29 wt % NH_3/ 71 wt. % H_2O solution

was commenced from the syringe. The addition rate was varied to give a

nominal concentration of NH_3 in the reducing gas between 0 (H_2-only) and 3.0

mole %. This condition was held for 1 hour. Then the reactor was allowed to

cool to room temperature in flowing hydrogen. After the reactor had cooled, the

hydrogen flow was replaced with a flow of 2:1 H_2:CO synthesis gas at 100 hr^{-1}

GHSV, for 15 minutes at atmospheric pressure. As with the hydrogen, the

synthesis gas was passed through a column of KOH pellets for removal of

impurities. Then valves were closed at the inlet and outlet of the reactor, storing

the catalyst under the synthesis gas.

Example 7 (Testing of Catalyst A)

The flow of synthesis gas into the reactor was resumed with the catalyst

of Example 6 (Catalyst A reduced with H_2+NH_3) at 100 hr^{-1} GHSV and 1 atm

pressure. Prior to entering the reactor, the synthesis gas was passed through a

column of KOH pellets (pellet diameter nominally 3-5 mm) for removal of

impurities. The synthesis gas composition was 2:1 H_2:CO by volume. The

reactor temperature was increased from room temperature to 160°C in about 40

minutes. This condition was held for 5 hours, after which the reactor was cooled

down to room temperature in the flowing synthesis gas and the catalyst stored

under the synthesis gas as described in Example 6. Testing was resumed the

next day following the same procedure, except that the test temperature was

10°C higher. This was repeated each day until the optimum operating

temperature was found. The optimum operating temperature was defined as the

temperature where the yield of C_{5+} products is maximized, as measured in gm of

- 14 -

C_{5+} product per standard cubic meter of synthesis gas fed to the reactor. Finding the optimum operating temperature entailed increasing the reactor temperature in 10°C steps until the C_{5+} yield decreased from the previous test. The temperature from the previous test is the optimum temperature. Catalyst performance was determined by measuring the gas contraction, product gas composition by gas chromatography, and C_{5+} liquid product yield. The C_{5+} liquid product was recovered form the reactor effluent using two traps. The first trap was water cooled and the second was cooled with dry ice/acetone (-80°C). The C_{5+} product in the first trap was weighted directly. The liquid product in the second trap was first warmed to room temperature, to vaporize C_{4-} components prior to weighing. The combined weights of the hydrocarbon liquid product in both traps was used to determine the C_{5+} product yield. The C_{5+} product from the optimum temperature was further analyzed, to determine hydrocarbon type and carbon chain length distribution. From time to time, the C_{5+} products from the non-optimum temperature tests were combined and analyzed. The catalyst precursor was not calcined prior to reduction in these experiments. The results are shown in Table 1 below.

Table 1

			Yield, gm/m^3 of Gas Feed		Selectivity, %		Alpha
Mole % NH$_3$ in Reducing Gas	Optimum Temp., °C	CO Conversion %	CH$_4$	C$_{5+}$	C$_{4-}$	C$_{5+}$	
0	200	60	26	78	40	60	0.8
0.5	210	45	9	76	37	76	0.84
0.75	210	49	24	70	43	57	0.85
1	210	58	21	72	42	58	0.84
2	200	42	10	72	20	80	0.84
3	210	24	4	40	25	75	0.85

- 15 -

These results demonstrate the effect on catalyst performance, of the NH_3 concentration in the reducing gas used to convert the precursor to the catalyst. Up to about 2 mole % NH_3 in the reducing gas, both the % CO conversion and C_{5+} yields are good, with the C_{5+} selectivity peaking at about 80%. Although the catalyst activity decreased when NH_3 was used in the reducing gas, the reduction is mainly from the C_{4-} gas products. The Schultz-Flory alpha also increased when the catalyst reducing gas contained NH_3 and stayed essentially constant from 0.5 to 3.0 mole % NH_3 in the reducing gas. These results show that the presence of NH_3 in the reducing gas during catalyst reduction, improved catalyst performance. Thus, in all cases, reduction in the presence of NH_3 increased the alpha of the hydrocarbon synthesis reaction. The greatest difference between having and not having NH_3 in the reducing gas, is seen for the run in which the H_2 reducing gas contained 0.5 mole % NH_3. This produced a C_{5+} selectivity of 76 %, with a high yield of C_{5+} hydrocarbons and only a 9 % methane make. At 2 mole % NH_3, the C_{5+} selectivity was even higher and the C_{5+} yield, while lower, was still good.

Example 8 (Catalyst B testing after Reduction with H_2 and then with H_2+NH_3)

The synthesis gas flow was resumed into the reactor with the catalyst of Example 5 (Catalyst B reduced first with H_2 then with H_2+NH_3) at 100 hr^{-1} GHSV and 1 atm pressure. Prior to entering the reactor, the synthesis gas was passed through a column of KOH pellets (pellet diameter nominally 3-5 mm) for removal of impurities. The synthesis gas composition was 2:1 H_2:CO by volume. The reactor temperature was increased from room temperature to 160°C in about 40 minutes. This condition was held for 5 hours, after which the reactor was cooled to room temperature in the flowing synthesis gas and the catalyst stored under the synthesis gas. Testing was resumed the next day

- 16 -

following the same procedure, except that the test temperature was 10°C higher.

This was repeated each day until the operating temperature was 190°C. At

190°C the catalyst performance was determined by measuring the gas

contraction, product gas composition by gas chromatography, and C_{5+} liquid

product yield. The C_{5+} liquid was recovered form the reactor effluent using two

traps. The first trap was water cooled and the second was cooled with dry

ice/acetone (-80°C). The C_{5+} product in the first trap was weighted directly.

The liquid product in the second trap was first warmed to room temperature to

vaporize C_{4-} components prior to weighing. The combined weights of the

hydrocarbon liquid product in both traps was used to determine the C_{5+} product

yield. The C_{5+} product from the optimum temperature was further analyzed to

determine hydrocarbon type and carbon chain length distribution. From time to

time, the C_{5+} products from the non-optimum temperature tests were combined

and analyzed. The catalyst precursor used in these experiments was calcined

prior to reduction. It should be noted that while the cobalt oxide formed by the

calcination converts to the metal during the reduction, the zirconium component

remains as the oxide and is not reduced to the metal. The results at 190°C are

shown in Table 2 below.

- 17 -

Table 2

Reduction Time, Hours*			Yield, gm/m^3 of Gas Feed		Selectivity, %		
H$_2$	H$_2$ + NH$_3$	CO Conversion %	CH$_4$	C$_{5+}$	C$_{4-}$	C$_{5+}$	Alpha
5	0	87	34	87	53	47	0.75
4	1	72	10	90	23	77	0.76
3	2	58	8	97	19	81	0.82
2	3	50	8	96	16	84	0.86
1	4	46	9	84	20	80	0.82
0	5	47	11	70	24	76	0.81

* Total reduction time of 5 hours in each case. Number in H$_2$ column is reducing time under hydrogen, before switching to a mixture of H$_2$ and NH$_3$ (5 mole %).

Table 2 shows how, at a constant reducing time of 5 hours, the performance of Catalyst B is affected by the presence of NH$_3$ in the H$_2$ reducing gas, when sequentially reduced with H$_2$ followed by H$_2$+NH$_3$, and also when reduced in only H$_2$+NH$_3$. It should be noted, that tests revealed optimum catalytic properties for the catalyst reduced under hydrogen, at a hydrogen treat gas ratio of 100 hr^{-1} GHSV, were achieved at a reduction time of five hours. This is why the total reduction time of 5 hours was chosen for this experiment. However, a portion of the metal reduction and concomitant activation is achieved in one hour. Thus, an active catalyst existed prior to contact with the hydrogen and ammonia reducing gas, for the runs in Table 2 above, in which the contact time with the hydrogen reducing gas was, 1, 2, 3 and 4 hours. In the last run in the Table, it was a precursor that was contacted with the hydrogen and ammonia mixture for 5 hours. Thus, this last run and the first run with only hydrogen reduction, are not within the scope of the invention and are presented for comparative purposes.

- 18 -

As Table 2 shows, in the second through the fifth runs, the precursor was at least partially reduced prior to contact with the hydrogen and ammonia mixture. With 4 hours on H_2, followed by only 1 hour on H_2+NH_3, a sharp increase in the C_{5+} yield and selectivity occurred, with a concomitantly sharp drop in methane make. Thus, Increasing the reduction time with H_2+NH_3 caused the C_{5+} yield, C_{5+} selectivity, and Schulz-Flory alpha to peak, between 2 to 4 hours of H_2+NH_3 reduction. Although the catalyst activity drops with increasing H_2+NH_3 reduction time, the activity drop is taken from the C_{4-} gas, leaving the yield of C_{5+} approximately constant up to three hours of the H_2/NH_3 treatment. More than three hours decreased the C_{5+} yield and selectivity, but the alpha of the reaction remained high. This shows that introduction of NH_3 into the reducing gas, during at least a portion of the catalyst reduction, is effective in improving catalyst performance.

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.

- 19 -

CLAIMS:

1. A process for enhancing the performance of a hydrocarbon synthesis catalyst comprises contacting said catalyst, comprising at least one catalytic metal component, with a reducing gas comprising a mixture of a hydrogen and ammonia, at catalyst reducing conditions.

2. A process according to claim 1 wherein, during hydrocarbon synthesis, said enhanced catalyst exhibits at least one property selected from the group consisting of (i) a C_{5+} selectivity greater than it otherwise would be if said catalyst had not been enhanced with said hydrogen and ammonia reducing gas mixture, (ii) a hydrocarbon synthesis reaction alpha greater than it would otherwise be if said catalyst had not been enhanced with said hydrogen and ammonia reducing gas mixture, and (iii) a methane make reduced to a level lower than it would otherwise be if said catalyst had not been enhanced with said hydrogen and ammonia reducing gas mixture.

3. A process according to claim 2 wherein said catalyst comprises a Fischer-Tropsch type of hydrocarbon synthesis catalyst.

4. A process according to claim 3 wherein wherein a portion of said at least one catalytic metal component is reduced to the catalytically active metal form, as a result of said contacting with said hydrogen and ammonia reducing gas.

5. A process according to claim 4 wherein said catalyst also comprises a metal oxide support component and wherein said catalytic metal component comprises at least one Group VIII metal.

- 20 -

6. A process according to claim 5 wherein wherein a portion of said at least one catalytic metal component is reduced to the catalytically active metal form, as a result of reduction in hydrogen without said ammonia.

7. A process according to claim 6 wherein said ammonia is present in said hydrogen reducing gas in an amount of from 0.01 to 15 mole % of the total reducing gas composition.

8. A process according to claim 9 wherein the hydrogen to ammonia mole ratio in said reducing gas comprising a mixture of hydrogen and ammonia ranges from 1000:1 to 5:1.

9. A process according to claim 8 wherein said catalytic metal component comprises at least one of Co and Ru and wherein said support component includes at least one selected from the group consisting of alumina, silica, alumino-silicates and titania.

10. A catalyst produced according to the process of claim 1.

11. A process for synthesizing hydrocarbons from a synthesis gas, which comprises a mixture of H_2 and CO, wherein said gas is contacted with an enhanced Fischer-Tropsch hydrocarbon synthesis catalyst at reaction conditions effective for said H_2 and CO in said gas to react and form hydrocarbons, wherein said enhanced catalyst comprises at least one catalytic metal component, and wherein said catalyst has been enhanced by contacting said catalyst with a reducing gas comprising a mixture hydrogen and ammonia at catalyst reducing conditions.

12. A process according to claim 11 wherein, during hydrocarbon synthesis, said enhanced catalyst exhibits at least one property selected from the

group consisting of (i) a C_{5+} selectivity greater than it otherwise would be if said catalyst had not been enhanced with said hydrogen and ammonia reducing gas mixture, (ii) a hydrocarbon synthesis reaction alpha greater than it would otherwise be if said catalyst had not been enhanced with said hydrogen and ammonia reducing gas mixture, and (iii) a methane make reduced to a level lower than it would otherwise be if said catalyst had not been enhanced with said hydrogen and ammonia reducing gas mixture.

13. A process according to claim 12 wherein said catalyst also comprises a metal oxide support component and wherein said catalytic metal component comprises at least one Group VIII metal.

14. A process according to claim 13 wherein a portion of said at least one catalytic metal component is reduced to the catalytically active metal form, as a result of said contacting with said hydrogen and ammonia reducing gas.

15. A process according to claim 14 wherein wherein a portion of said at least one
catalytic metal component is reduced to the catalytically active metal form, as a result of reduction in hydrogen without said ammonia.

16. A process according to claim 15 wherein said ammonia is present in said hydrogen
reducing gas in an amount of from 0.01 to 15 mole % of the total reducing gas composition and wherein said hydrogen to ammonia mole ratio in said reducing gas ranges from 1000:1 to 5:1.

17. A process according to claim 16 wherein said support component includes at least one selected from the group consisting of alumina, silica, alumino-silicates and titania.

18. A process according to claim 19 wherein said activated catalyst is in a fluidized bed, a fixed bed or dispersed in a slurry liquid during said hydrocarbon synthesis and wherein at least a portion of said synthesized hydrocarbons are upgraded by one or more operations comprising fractionation and/or one or more conversion operations.

19. A process according to claim 18 wherein at least a portion of said hydrocarbons being upgraded are solid at standard conditions of room temperature and pressure.

20. A slurry hydrocarbon synthesis process according to claim 19 wherein said catalytic metal component includes at least one of Co and Ru.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C10G2/00   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   C10G   C07C   B01J

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 728 602 A (RHEINPREUSSEN AG FÜR BERGBAU UND CHEMIE) 20 April 1955 (1955-04-20)	1,10,11
A		3-6,9, 13-15
	claims 1,16 page 1, line 71 - line 76	
X	US 4 565 831 A (PIRKLE JR JAMES C ET AL) 21 January 1986 (1986-01-21)	1,10
A	claims 1,7 column 6, line 39 - line 44	4,5
A	US 4 196 100 A (AHMAD UMAR M U ET AL) 1 April 1980 (1980-04-01) claims 1,5,20,21 column 9, line 28 - line 29	1,3-6, 9-11

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

[X] 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

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 April 2001	23/04/2001

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 728602 A	20-04-1955	NONE	
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US 4196100 A	01-04-1980	CA 1118400 A US 4397964 A	16-02-1982 09-08-1983