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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 May 2012 (24.05.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/068164 A2

(51) International Patent Classification:
B01J 37/02 (2006.01) *B01J 19/00* (2006.01)
B01J 23/745 (2006.01) *C07C 1/04* (2006.01)
C10G 2/00 (2006.01)

(21) International Application Number:
PCT/US2011/060857

(22) International Filing Date:
15 November 2011 (15.11.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/415,726 19 November 2010 (19.11.2010) US

(71) Applicant *(for all designated States except US)*: **RENTECH, INC.** [US/US]; 10877 Wilshire Blvd., Suite 600, Los Angeles, California 90024 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **WRIGHT, Harold** [US/US]; 1305 Indian Paintbrush Lane, Longmont, Colorado 80503 (US). **DEMIREL, Belma** [US/US]; 979 Wolf Creek Drive, Longmont, Colorado 80501 (US). **FERDOUS, Deena** [CA/US]; 6985 S. Addison Ct., Aurora, Colorado 80016 (US). **TAYLOR, Jesse W.** [US/US]; 3402 Van Wie Dr. E., Baldwinsville, New York 13027 (US). **DUVENHAGE, Dawid E.** [ZA/US]; 27218 Mountain Park Rd., Evergreen, Colorado 80439 (US). **ROLFE, Sara L.** [US/US]; 3715 Lincoln Ct., Loveland, Colorado 80538 (US).

(74) Agent: **WESTBY, Timothy S.**; Porter Hedges LLP, P.O. Box 4078, Houston, Texas 77210-4078 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: PROTECTED FISCHER-TROPSCH CATALYST AND METHODS OF MAKING AND USING SAME

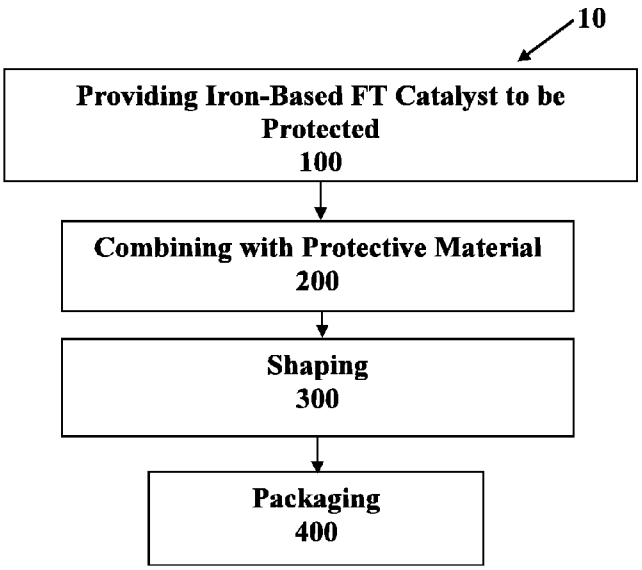

FIG. 1

(57) Abstract: A method of providing a protected Fischer-Tropsch catalyst by providing catalyst particles functional for catalyzing the Fischer-Tropsch synthesis reaction, combining the catalyst particles with a protective material such that the catalyst particles are coated with the protective material, and shaping the combination comprising catalyst and protective material to provide the protected catalyst. A method for providing protected Fischer-Tropsch catalyst by fluidizing a bed of catalyst particles having FT functionality, reducing the catalyst particles by contacting the catalyst particles with reducing gas under reducing conditions, activating the reduced catalyst particles by contacting the reduced catalyst particles with an activation gas under activation conditions, combining the activated catalyst, under inert or carbiding atmosphere, with molten wax, whereby the catalyst particles are coated with wax and shaping the wax-coated catalyst particles to provide the protected catalyst. Catalysts produced via the methods are also provided.

WO 2012/068164 A2

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

Protected Fischer-Tropsch Catalyst and Methods of Making and Using Same

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not applicable.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

BACKGROUND

Field of the Invention

[0003] This invention relates generally to the field of Fischer-Tropsch (FT) catalysts. More particularly, the invention relates to a protected FT catalyst and methods of preparing and utilizing same. Even more particularly, the invention relates a method of preparing a protected iron-based Fischer-Tropsch catalyst and a method of producing synthetic hydrocarbons therewith.

Background

[0004] Fischer-Tropsch (FT) synthesis catalytically converts synthesis gas comprising H_2 and CO (also known as 'syngas') to aliphatic hydrocarbon products. The FT synthesis, which is a catalytic reaction catalyzed by numerous Fischer-Tropsch catalysts known in the art, produces aliphatic hydrocarbons ranging from methane to paraffinic waxes having up to 100 carbon atoms or more.

[0005] Although Fischer-Tropsch synthesis exhibits fast surface reaction kinetics, the overall reaction rate is significantly heat and mass transfer limited in conventional reactors such as tubular fixed bed reactors and slurry reactors. These heat and mass transfer limitations reduce the choice of operating conditions. Limited heat transfer along with rapid surface reaction kinetics can produce hot spots in catalysts beds. Hot spots undesirably promote methane formation, reduce the heavy hydrocarbon selectivity and deactivate the catalyst. Strong mass transfer resistance inherent in suspended catalyst in a slurry system generally reduces the effective reaction rate and also presents the challenge of separating the catalyst from the hydrocarbon products.

[0006] Conventionally, fixed bed reactors with small internal diameters and slurry or fluidized bed reactors operated with small catalyst particles have been utilized to address the heat and mass transfer limitations.

[0007] For use in fixed bed reactors, larger catalyst, for example iron catalyst having an average size in the range of from about 2 to about 3 mm, has conventionally been reduced (*e.g.* in hydrogen) and coated (*e.g.* in wax) for protection from oxidation, for example during transport to

activation reactors and/or loading into an on-site activation reactor. The coating process reduces the risks associated with transport of the catalyst and/or loading of a fixed or fluidized bed reactor therewith. The catalyst is subsequently activated (*e.g.* with carbon monoxide, hydrogen or synthesis gas) to form an active (*e.g.* carbidic) phase. Such a coating procedure is challenging, however, with spray-dried catalyst particles which have a smaller particle size (*e.g.* an average particle size of less than about 300 microns) and thus substantially different flow properties from their larger counterparts. Such small spray-dried catalyst particles may readily combust when oxygen is present, and, thus, removing such particles from a reduction reactor can create a highly reactive catalyst dust. Additionally, it is generally not desirable and may not even be feasible to simply combine such small catalyst particles with a protective coating material (*e.g.* wax) under gravity (*e.g.* by dumping or pouring the catalyst particles into a vessel containing the protective coating).

[0008] Accordingly, there is an outstanding need in the industry for improved methods of protecting spray-dried catalysts (*e.g.* from oxidation) during transport and/or reactor loading. Desirably, such a method provides a protected spray-dried catalyst that has been activated prior to being protected (*i.e.* covered) with a protective material. Via such methods, activated catalyst can be made readily available for loading into a reactor, thus reducing reaction equipment and/or process time. For example, utilizing such protected pre-activated spray-dried catalyst, no on-site dedicated activation vessels may be required and/or no or less time may be lost during production due to on-site activation. The protective coating can desirably be removed (*e.g.* melted) from coated pre-activated catalyst particles within a production reactor or removed from the protected catalyst in another vessel or reactor prior to introduction of the activated catalyst into a production reactor.

SUMMARY

[0009] Disclosed herein is a method of providing a protected Fischer-Tropsch catalyst by providing catalyst particles functional for catalyzing the Fischer-Tropsch synthesis reaction; combining the catalyst particles with a protective material such that the catalyst particles are coated with the protective material; and shaping the combination comprising catalyst and protective material to provide the protected catalyst. In embodiments, the catalyst is a spray-dried catalyst. In embodiments, the spray-dried catalyst is a precipitated iron-based catalyst.

[0010] In embodiments, the method further comprises introducing the protected catalyst into a reactor. The reactor can be a Fischer-Tropsch synthesis reactor.

[0011] In embodiments, the method further comprises fluidizing the catalyst particles, to provide a fluidized bed. Fluidizing can comprise introducing an inert gas into a vessel containing the

catalyst particles. In embodiments, the method further comprises reducing the catalyst particles. Reducing can comprise contacting the fluidized catalyst particles with reducing gas at a reduction temperature. In embodiments, the reducing gas comprises at least one component selected from the group consisting of hydrogen, carbon monoxide and synthesis gas. In embodiments, contacting the fluidized catalyst particles with reducing gas is performed at a reducing temperature in the range of from about 200°C to about 350°C for a time in the range of from about 4 hours to about 48 hours.

[0012] In embodiments, the method further comprises contacting the catalyst particles with activation gas under activation conditions, whereby the catalyst particles are carbided. In embodiments, the method further comprises slumping the fluidized bed prior to combining the catalyst particles with protective material.

[0013] In embodiments, the method further comprises activating the catalyst by contacting the catalyst with activation gas. In embodiments, activating is performed prior to combining the catalyst particles with protective material. In embodiments, activating is performed subsequent to shaping. In embodiments, activating further comprises introducing the protected catalyst into an activation reactor, melting the protective material, and contacting the catalyst with an activation gas. In embodiments, the activation reactor is a dedicated activation reactor. In embodiments, the activation reactor is the production reactor. The activation gas can be selected from the group consisting of synthesis gas, carbon monoxide, hydrogen and combinations thereof.

[0014] In embodiments, shaping the catalyst to provide protected catalyst comprises shaping the coated catalyst into shapes selected from substantially spherical, oblong, tabletted, cylindrical, and combinations thereof. In embodiments, the catalyst particles have an average size of less than about 150μm. In embodiments, the protective material comprises wax. In embodiments, the wax is selected from the group consisting of poly alpha olefin waxes and Fischer-Tropsch waxes. In embodiments, the protective coating comprises FT wax.

[0015] Also disclosed herein is a method for providing protected Fischer-Tropsch catalyst by fluidizing a bed of catalyst particles having FT functionality; reducing the catalyst particles by contacting the catalyst particles with reducing gas under reducing conditions; activating the reduced catalyst particles by contacting the reduced catalyst particles with an activation gas under activation conditions; combining the activated catalyst, under inert or carbiding atmosphere, with molten wax, whereby the catalyst particles are coated with wax; and shaping the wax-coated catalyst particles to provide the protected catalyst. The method can further comprise introducing the shaped wax-coated catalyst into a reactor. The method can further comprise melting the wax from the shaped wax-coated catalyst in the reactor to provide a catalyst slurry and introducing the

catalyst slurry into a production reactor. In embodiments, the reactor is a production reactor. The method can further comprise operating the production reactor at a temperature above that at which the wax melts. In embodiments, the production reactor is an FT synthesis reactor.

[0016] Also disclosed herein is the catalyst formed via the disclosed method.

[0017] The foregoing has outlined rather broadly the features and technical advantages of the invention in order that the detailed description of the invention that follows may be better understood. Additional objects, embodiments, features and advantages of the invention will be apparent from the following detailed description of the invention and the appended claims. It should be appreciated by those skilled in the art that the conception and the specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] For a detailed description of the preferred embodiments of the invention, reference will now be made to the accompanying drawings wherein:

[0019] FIGURE 1 is a block flow diagram of a method of providing protected iron-based FT catalyst according to an embodiment of this disclosure;

[0020] FIGURE 2 is a block flow diagram of a method of providing iron-based FT catalyst to be protected according to an embodiment of this disclosure;

[0021] FIGURE 3 is a block flow diagram of a method of reducing and/or activating an iron-based FT catalyst according to an embodiment of this disclosure;

[0022] FIGURE 4 is a block flow diagram of a method of combining an iron-based FT catalyst with protective material according to an embodiment of this disclosure;

[0023] FIGURE 5 is a block flow diagram of a method of shaping according to an embodiment of this disclosure; and

[0024] FIGURE 6 is a schematic of an apparatus suitable for use in providing protected iron-based FT catalyst according to an embodiment of this disclosure.

NOTATION AND NOMENCLATURE

[0025] Certain terms are used throughout the following description and claim to refer to particular system components. This document does not intend to distinguish between components that differ in name but not function.

[0026] As used herein, the term 'wax' is used to refer to hydrocarbons that are solid at ambient temperature. Characteristically, such hydrocarbons can have a melting point in excess of about 80°C.

DETAILED DESCRIPTION

[0027] ***Overview.*** Herein disclosed are a protected, FT catalyst, a method of making such a protected, FT catalyst and a method of providing such a protected, FT catalyst to a catalytic process. Although disclosure hereinbelow will be made with reference to iron-based Fischer-Tropsch catalyst, it is to be understood that the disclosed method of protecting catalyst is suitable for use with other spray-dried catalysts as well. For example, the method may be suitable for use with FT catalysts that are based on metal(s) other than or in addition to iron and/or to catalysts other than FT catalysts. Although the disclosed methods may be especially suitable for protecting catalysts that are susceptible to deactivation in the presence of air, such as, for example, reduced FT catalysts, the method may also be beneficial for use with small (e.g. spray dried) catalysts that do not need protection from the environment, as such 'protection' may aid in the handling of such small spray-dried catalysts. For example, coating spray-dried catalyst can facilitate handling during transport from a manufacturing location on or off-site to a catalyst utilization site.

[0028] In embodiments, precipitated catalyst is to a process for production of product utilizing the catalyst via the disclosed method. The process can utilize the catalyst in a fixed bed, a packed bed, a fluidized bed, a slurry bubble column reactor (SCBR) or a combination of two or more thereof. In embodiments, the disclosed method facilitates reduction and/or activation of a spray-dried precipitated iron catalyst and/or transportation of such a catalyst to a production reactor. The disclosed method may be superior to conventional processes, providing easier (*i.e.* simpler and/or less hazardous) handling of catalyst during catalyst transportation and/or reactor loading.

[0029] As discussed further hereinbelow, in embodiments, the disclosed method is operable to protect a spray-dried catalyst with a wax coating. The coated catalyst may be pelletized to provide for facilitated reactor loading. In embodiments, the catalyst is coated and pelletized subsequent to activation of the catalyst, allowing reduced start-up time, by eliminating the need for further activation prior to use. Providing a protected pre-activated catalyst according to embodiments of the disclosed method can eliminate the need for a dedicated catalyst activation reactor at an FT plant site, thus potentially reducing the overall capital cost of an FT plant. In alternative embodiments discussed further hereinbelow, catalyst particles are coated with wax and pelletized prior to activation. In such instances, coating allows for easier handling (*e.g.* catalyst transportation and/or loading of catalyst into a reactor), and activation may be performed *in situ* in an FT reactor prior to start-up or in a dedicated activation reactor prior to introduction into an FT production

reactor. As discussed further hereinbelow, the disclosed method of protecting catalyst can comprise sequential reduction, activation and protection of the catalyst.

[0030] ***Method of Preparing Protected Catalyst.*** A method of preparing a protected catalyst will now be described with reference to Figure 1, which is a block flow diagram of a method 10 of providing protected catalyst according to an embodiment of this disclosure. Method 10 comprises: providing iron-based FT catalyst to be protected at 100; combining the catalyst with protective material at 200; and shaping the protective material/catalyst combination at 300. The method may further comprise packaging the protected shaped catalyst for transport, as indicated at 400.

[0031] In embodiments, the catalyst to be protected is an FT catalyst known in the art. In embodiments, the catalyst to be protected is an FT catalyst having an average particle size in the range of from about 40 μm to about 150μm, from about 40 μm to about 125 μm, from about 40 μm to about 100 μm, or from about 30 μm to about 80 μm. In embodiments, the catalyst to be protected has an average particle size of less than 300, 250, 200, 150, 100, 95, 90, 85 or 80 μm; such catalyst can have an average particle size of greater than 5, 10, 20, 30, 40, 50 or 60 μm, all-inclusive (*e.g.* from about 30 to about 200 μm or from about 10 to about 150 μm). The catalyst to be protected may be a precipitated spray-dried iron-based catalyst suitable for use in an FT production reactor. The FT production reactor can be a slurry-phase, a packed bed, a fluidized bed and/or a fixed bed reactor.

[0032] ***FT Catalyst.*** Providing catalyst particles at 100 may comprise providing a spray-dried FT catalyst known in the art to be suitable for catalyzing the FT synthesis reaction (*i.e.* conversion of carbon monoxide and hydrogen into C_{2+} hydrocarbons). In embodiments, providing catalyst particles at 100 comprises providing spray-dried precipitated FT catalyst. In embodiments, the Fischer-Tropsch catalyst is a metal-based catalyst. In embodiments, the FT catalyst comprises a precipitated iron catalyst suitable for use in Fischer Tropsch synthesis.

[0033] The precipitated FT catalyst can be selected from the group consisting of iron-based FT catalysts, cobalt based FT catalysts and combinations thereof. In embodiments, the Fischer-Tropsch catalyst is an iron carbide catalyst. The catalyst to be protected can comprise at least one catalytic metal (*i.e.* Co, Fe) at a loading level of about 20% by weight or more, about 25% by weight or more, about 28% by weight or more, about 30% by weight or more, about 32% by weight or more, about 35% by weight or more, about 37% by weight or more, or about 40% by weight or more. The catalyst can comprise at least one catalytic metal (*i.e.* Co, Fe) at a loading level of in the range of from about 20% by weight to about 70% by weight, from about 30% by weight to about 60% by weight, or from about 20% by weight to about 60% by weight. In embodiments, the catalyst is an iron-based FT catalyst comprising from about 20 to about 70

weight percent iron, from about 4 to about 30 weight percent iron, from about 6 to about 25 weight percent iron or from about 8 to about 20 weight percent iron.

[0034] In embodiments, the catalyst comprises at least one catalytically active metal or oxide thereof. In embodiments, the catalyst further comprises a catalyst support. In embodiments, the catalyst further comprises at least one promoter. The catalytically active metal may be selected from the group consisting of Co, Fe, Ni, Ru, Re, Os, and combinations of two or more thereof. The support material may comprise alumina, zirconia, titania, magnesia, silica, zeolite, aluminum fluoride, fluorided alumina, bentonite, ceria, zinc oxide, silica-alumina, silicon carbide, a molecular sieve, or a combination of two or more thereof. The support material may comprise a refractory oxide. The promoter may be selected from Group IA, IIA, IIIB or IVB metals and oxides thereof, lanthanide metals and metal oxides, and actinide metals and metal oxides. In embodiments, the promoter is selected from the group consisting of Li, B, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, La, Ac, Ti, Zr, La, Ac, Ce and Th, oxides thereof, and mixtures of two or more thereof. The catalyst to be protected may be selected from catalysts disclosed in U.S. Pat. Nos. 4,585,798; 5,036,032; 5,733,839; 6,075,062; 6,136,868; 6,262,131; 6,353,035; 6,368,997; 6,476,085; 6,451,864; 6,490,880; 6,648,662; 6,537,945; 6,558,634; and U.S. Patent App. No. 2003/0105171; these patents and patent applications hereby incorporated herein by reference for their disclosures of Fischer-Tropsch catalysts and methods for preparing such catalysts.

[0035] In embodiments, the FT catalyst is an iron-based catalyst formed as described in or having the composition of FT catalyst described in U.S. Patent No. 5,508,118 and U.S. Patent Applications No. 12/189,424; 12/198,459; 12/207,859; 12/474,552; and/or 12/790,101, the disclosure of each of which is hereby incorporated herein in its entirety for all purposes not contrary to this disclosure.

[0036] Providing iron-based FT catalyst at 100 can comprise precipitating an iron-based FT catalyst as described, for example in any of the above-incorporated patent applications.

[0037] In embodiments, the catalyst protected via this disclosure is an iron-based catalyst comprising iron, copper and potassium in a weight ratio of 100 Fe : 1 Cu : 1 K (wt%:wt%:wt%). In embodiments, the catalyst is an iron catalyst comprising at least one selected from hematite, maghemite and ferrihydrite. In embodiments, the catalyst comprises maghemite and hematite with a weight ratio of maghemite : hematite in the range of form about 1% : 99% to about 70% : 30%. In embodiments, the iron catalyst has a weight ratio of maghemite to hematite of about 10% : 90%. The catalyst can have a particle size distribution in the range of 10 μm – 150 μm. The catalyst can exhibit a BET surface area in the range of from about 45 m^2/g to about 250 m^2/g or from about 45 m^2/g to about 180 m^2/g. The catalyst can have a mean pore diameter in the range of from about 45

Å to about 120 Å or from about 75 Å to about 120 Å. The catalyst can have a mean pore volume in the range of from about 0.2 cc/g to about 0.6 cc/g or from about 0.20 cc/g to about 0.24 cc/g. The catalyst can have a mean crystallite size in the range of from about 15 nm to about 40nm or from about 25 nm to about 29 nm.

[0038] Depending on the preselected alpha, *i.e.* the polymerization probability desired, a precipitated iron catalyst protected via this disclosure may have a weight ratio of potassium (*e.g.* as carbonate, bicarbonate, oxide and/or hydroxyl) to iron (K:Fe) in the range of from about 0.005 and about 0.015, more preferably in the range of from 0.0075 to 0.0125, and most preferably about 0.010. Greater amounts of alkali metal promoter (*e.g.* potassium) may cause the product distribution to shift toward the longer-chain molecules, while lesser amounts of alkali metal may result in a predominantly gaseous hydrocarbon product, so the catalyst composition can be based on the desired FT products, in embodiments.

[0039] The weight ratio of copper to iron in the iron Fischer-Tropsch catalyst protected via this disclosure may be in the range of from about 0.005 and 0.050, from about 0.0075 and 0.0125, or may be about 0.010. The copper may serve as an induction promoter. In embodiments, the weight ratio of Cu:Fe in the catalyst protected via this disclosure is in the range of from about 1:100 to about 20:100. In embodiments, the weight ratio of Cu:Fe in the catalyst protected via this disclosure is at least or about 1, 5, 10, 15 or 20:100.

[0040] The catalyst protected via this disclosure may be an iron Fischer-Tropsch catalyst comprising structural promoter. The structural promoter may significantly reduce the breakdown of the catalyst when utilized in a SBCR (slurry bubble column reactor). The structural promoter may comprise silica, and the silica may serve to enhance the structural integrity of the catalyst during activation of and/or operation with the catalyst. In embodiments, the catalyst protected via the disclosed method comprises a mass ratio of SiO_2:Fe of less than about 1:100 when the structural promoter comprises silica and less than about 50:100, 25:100 or 8:100 when the structural promoter comprises silica sol.

[0041] In embodiments, the at least one structural promoter is selected from oxides of metals and metalloids and combinations thereof. The structural promoter may be referred to as a binder, a support material, or a structural support.

[0042] Depending on the level of structural promoter comprising silicate and the preselected alpha, *i.e.* the polymerization probability desired, the weight ratio of K:Fe may be from about 0.5:100 to about 6.5:100, from about 0.5:100 to about 2:100, or about 1:100.

[0043] In embodiments wherein the structural promoter comprises silica sol, the weight ratio of iron to potassium is in the range of from about 100:1 to about 100:5. In embodiments, the weight

ratio of iron to potassium is in the range of from about 100:2 to about 100:6. In embodiments, the weight ratio of iron to potassium is in the range of from about 100:3 to about 100:5. In embodiments, the weight ratio of iron to potassium is in the range of from about 100:4 to about 100:5. In some preferred embodiments, the weight ratio of iron to potassium is in the range of from about 100:2 to about 100:4. In embodiments, the weight ratio of iron to potassium about 100:3. In embodiments, the weight ratio of iron to potassium is about 100:5.

[0044] In embodiments wherein the structural promoter comprises silica sol, the weight ratio of iron to copper may be in the range of from about 100:1 to about 100:20. In some embodiments, the weight ratio of iron to copper is in the range of from about 100:1 to about 100:10. More preferably, the weight ratio of iron to copper is in the range of from about 100:1 to about 100:8. Still more preferably, the weight ratio of iron to copper is in the range of from about 100:3 to about 100:5. In some preferred embodiments, the weight ratio of iron to copper is in the range of from about 100:2 to about 100:4. In embodiments, the weight ratio of iron to copper is about 100:5. In embodiments, the weight ratio of iron to copper is about 100:3.

[0045] Broadly, in embodiments, wherein the structural promoter is silica sol, the iron to SiO_2 weight ratio may be in the range of from about 100:1 to about 100:8; alternatively, in the range of from 100:1 to 100:7. In embodiments, wherein the structural promoter is silica, the iron to SiO_2 weight ratio may be in the range of from about 100:2 to about 100:6. In embodiments, the weight ratio of iron to silica is in the range of from about 100:3 to about 100:5. In embodiments, wherein the structural promoter is silica, the iron to SiO_2 weight ratio is about 100:5. In embodiments, wherein the structural promoter is silica, the iron to SiO_2 weight ratio is in the range of from about 100:3 to about 100:7; alternatively, in the range of from about 100:4 to about 100:6. In embodiments, the catalyst protected via this disclosure comprises an Fe:Cu:K:SiO_2 mass ratio of about 100:4:3:5.

[0046] In embodiments, the catalyst protected via this disclosure is a cobalt FT catalyst comprising from about 4 to about 30 weight percent cobalt, from about 6 to about 25 weight percent cobalt or from about 8 weight percent to about 20 weight percent cobalt.

[0047] In embodiments, the catalyst comprises cobalt, and optionally a co-catalyst and/or promoter, supported on a support wherein the cobalt loading is at least or about 5, 10, 15, 20, 25, 28, 30, 32, 35, or 40 percent by weight. In embodiments, the cobalt loading is in the range of from about 5 to about 50% by weight, from about 10 to about 50% by weight, from about 15 to about 50% by weight, from about 20 to about 50% by weight, from about 25 to about 50% by weight, from about 28 to about 50% by weight, from about 30 to about 50% by weight, or from about 32 to about 50% by weight. The metal dispersion for the catalytically active metal (*e.g.* Co, and

optionally co-catalyst and/or promoter) of the catalyst may be in the range of from about 1 to about 30%, from about 2 to about 20%, or from about 3 to about 20%. In embodiments, the co-catalyst is selected from the group consisting of Fe, Ni, Ru, Re, Os, oxides thereof, and mixtures of two or more thereof. In embodiments, the catalyst further comprises at least one promoter selected from the group consisting of Group IA, IIA, IIIB or IVB metals, oxides thereof, lanthanide metals and oxides thereof, and actinide metals and oxides thereof. In embodiments, the promoter is selected from the group consisting of Li, B, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, La, Ac, Ti, Zr, La, Ac, Ce, Th, oxides thereof, and mixtures of two or more thereof. The co-catalyst may be employed at a concentration in the range of from about 0 to about 10% by weight based on the total weight of the catalyst (*i.e.*, the weight of catalyst, co-catalyst, promoter and support) or from about 0.1 to about 5% by weight. The promoter may be employed at a concentration of up to about 10% by weight based on the total weight of the catalyst, and in one embodiment about 0.1 to about 5% by weight.

[0048] In embodiments, the catalyst protected via this disclosure comprises cobalt supported by alumina; the loading of cobalt is at least about 25% by weight, at least about 28% by weight, at least about 30% by weight, or at least about 32% by weight; and the cobalt dispersion is at least about 3%, at least about 5%, or at least about 7%.

[0049] In embodiments, the catalyst provided at 100 is spray-dried form of the FT catalyst described in and/or formed via the multiple impregnation step method described in U.S. Patent No. 7,084,180, the disclosure of which is hereby incorporated herein in its entirety for all purposes not contrary to this disclosure.

[0050] ***Spray-Drying.*** In embodiments, providing catalyst at 100 comprises spray-drying by any means known in the art. In embodiments, providing catalyst at 100 comprises spray-drying a precipitated FT catalyst by any means known in the art.

[0051] Methods known to those of skill in the art may be used to spray dry FT catalyst particles to be protected via this disclosure. For example, a Niro dryer may be used to perform spray drying. Spray drying as defined herein, is the process of drying a liquid feed through a hot gas. In embodiments the catalyst slurry fed to the spray dryer is a solution, a colloid, or a suspension. In embodiments, the spray-dried catalyst particles are smooth substantially round (or spherical) catalyst particles. In embodiments, the spray-dried catalyst particles are rough and/or non spherical, catalyst particles. Smooth, round particles may be particularly desirable because such particles may inhibit catalyst attrition due to increased particle density. Apart from contributing structural integrity, the presence of structural support/promoter (*e.g.* silica) in iron slurries may assist in spraying smooth round catalyst particles. The density of sprayed particles depends upon the solids content of the feed to be spray-dried. In embodiments, the catalyst slurry to be spray-

dried has a solids content of from about 1% to about 50%. In embodiments, the catalyst slurry to be spray-dried has a solids content of from about 10% to about 30% or from about 0.5% to about 12.5%.

[0052] In embodiments, the spray dryer outlet temperature is controlled at a temperature of from 90°C to about 200°C or from about 90°C to about 110°C. In embodiments, the spray dryer temperature is controlled at a temperature of from 95°C to about 100°C. In some embodiments, the spray dryer temperature is controlled at a temperature of from about 104°C to about 108°C. In embodiments, the spray-dried particles have a Gaussian type particle size distribution (PSD). In embodiments, a precipitated catalyst slurry is spray dried to provide microspheric particles in the size range of 30 to 100 or 30 to 90 micrometers. In embodiments, the mean particles size of the spray-dried catalyst is in the range of from about 30 to about 90 μm, in the range of from about 40 μm to about 150 μm or in the range of from about 40 μm to about 100 μm. In embodiments, the mean particle size is in the range of from about 38μm to about 80μm. In embodiments, the mean particles size is in the range of from about 36μm to about 48μm. In embodiments, the spray-dried catalyst particles have an average particle size of about 80 micrometer.

[0053] As mentioned hereinabove, spray drying can be performed with a Type H Mobil Niro Spray Dryer. Such a spray dryer comprises a two-fluid nozzle atomizer, drying chamber, air disperser, main chamber, product collection section, air ducts, cyclone, exhaust fan, air heater, and instrument panel. A feed slurry can be introduced to the spray dryer through a nozzle from the bottom with drying air cross-flowing from the top. The feed slurry can comprise from about 10 to about 50 weight percent solids, from about 12 to about 30 weight percent solids, from about 20 to about 25 weight percent solids, or about 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24 or 25 weight percent solids. In embodiments, the solids content of the slurry prior to addition of promoter is in the range of from about 10 wt% to about 20 wt%, or about 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt%. In embodiments, the solids content of the slurry after addition of promoter is in the range of from about 10 wt% to about 20 wt%, or about 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt%.

[0054] The spray drying conditions can comprise an inlet temperature in the range of from about 350°C to about 450°C or about 350°C, 360°C, 370°C, 380°C, 390°C, 400°C, 410°C, 420°C, 430°C, 440°C or 450°C. The outlet temperature can be in the range of from about 70°C to about 100°C or about 70°C, 73°C, 75°C, 77°C, 80°C, 85°C, 90°C, 95°C, 96°C. The water setup flow can be about 4.0 to 4.5 kg/hr (feed flow can be set with water and subsequently switched to the actual slurry feed). The atomizer air flow can be about 1 bar with a 30% setting on a variable area flow meter. Coarse and fine samples can be collected.

[0055] As indicated in Figure 2, which is a block flow diagram of a method 100A of providing catalyst to be protected according to an embodiment of this disclosure, providing catalyst can comprise reducing and/or activating a spray-dried catalyst 110.

[0056] As indicated in Figure 3, which is a block flow diagram of a method 110A of reducing and/or activating a catalyst according to an embodiment of this disclosure, reducing and/or activating a catalyst can comprise fluidizing a bed of spray-dried catalyst at 115 and contacting the fluidized catalyst with a reducing gas, contacting the catalyst with an activating gas or both contacting the catalyst with a reducing gas and then contacting the reduced catalyst with an activating gas at 117. Fluidizing an amount of catalyst at 115 can comprise introducing a volume of catalyst into a fluidized bed reactor and fluidizing the bed of catalyst by introduction of a fluidizing gas into the fluidized bed reactor. The fluidization gas can be selected from the group consisting of carbon monoxide, hydrogen, nitrogen, synthesis gas, and combinations thereof.

[0057] ***Calcining.*** Catalyst preparation method 110A may comprise calcining. To minimize aging, spray dried catalyst may be calcined immediately following spray drying, in embodiments. In embodiments, the spray dried catalyst is calcined at a temperature in the range of from about 200°C to about 600°C, from about 280°C to about 600°C, from about 300°C to about 600°C or from about 200°C to about 400°C. In embodiments, spray dried catalyst is calcined at a temperature in the range of from about 300°C to about 380°C. In embodiments, spray dried catalyst is calcined at a temperature of about 300°C. In embodiments, spray dried catalyst is calcined at a temperature of about 320°C. In embodiments, spray dried catalyst is calcined at a temperature of about 380°C. Calcination may be performed for a time period in the range of from about 4 to about 10 hours. In embodiments, the spray dried catalyst is calcined by heating to a temperature of about 380°C by heating at a rate of 30°C per minute and calcined for 4 hours. In embodiments, the spray dried catalyst is calcined by heating to a temperature of about 380°C by heating at a rate of about 1°C per minute and calcined for 4 hours. In embodiments, the spray dried catalyst is calcined by heating to a temperature of about 300°C by heating at a rate of from about 0.5°C per minute to about 2°C per minute. The spray dried catalyst may be calcined at the calcination temperature for about 4 hours. In embodiments, the spray dried catalyst is calcined by heating to a calcination temperature by heating at a rate in the range of from about 1°C to about 30°C per minute and calcined for a calcination duration. In embodiments, the heating rate is in the range of from about 0.5°C/min to about 25°C/min, from about 1°C/min to about 20°C/min or from about 1°C/min to about 15°C/min, from about 1°C/min to about 10°C/min, from about 1°C/min to about 9°C/min or from about 1°C/min to about 8°C/min, 7°C/min, 6°C/min, 5°C/min, 4°C/min, 3°C/min or 2°C/min. In embodiments, the spray dried catalyst is

calcined in an oven or in a calciner, in atmosphere. As known in the art, spray dried catalyst may be calcined in, for example, a porcelain crucible.

[0058] In embodiments, the precipitated particles are stabilized (prestabilized) by heating to a temperature lower than the calcination temperature prior to calcination. In embodiments, the spray dried catalyst is prestabilized at a temperature below the temperature at which phase related changes/structuring take place [this may, for example, be determined by differential temperature analysis (DTA) over a temperature range, for example room temperature (RT) to about 550°C].

[0059] In embodiments, the spray dried catalyst is prestabilized at a temperature below this phase change temperature prior to calcination. It is proposed that the Si-O-Si-K species introduced into the iron slurry undergoes dramatic restructuring on drying. In embodiments, water is used sparingly to inhibit shrinking of the catalyst on drying. In embodiments, a stepwise increase in calcination temperature is used to prevent/minimize reduction in surface area. For instance, in embodiments, the catalyst is prestabilized by heating at a first (relatively low) temperature prior to calcination at a (relatively high) calcination temperature. In embodiments, the catalyst is prestabilized at a temperature in the range of from about 100°C to about 150°C. In embodiments, the spray dried catalyst is prestabilized at a temperature in the range of from about 120°C to about 150°C. In embodiments, spray dried catalyst is prestabilized overnight, before increasing to full calcinations conditions, to set the catalyst structure. Without wishing to be limited by theory, prestabilizing the precipitated catalyst at a lower temperature prior to calcination may minimize pore loss to a loss of micropores upon calcining, resulting in improved catalyst surface area.

[0060] In specific embodiments the catalyst is prestabilized at 140°C for 4 hours, the temperature is increased at a rate in the range of from about 0.5°C/min to about 2°C/min to a temperature of greater than about 200°C and the catalyst calcined for 4 hours, the temperature is then increased at a rate in the range of from about 0.5°C/min to about 2°C/min, and the catalyst calcined at 300°C for 4 hours. In some embodiments, the catalyst is calcined at a temperature of about 320°C for a period of about 4 hours. In certain embodiments, the catalyst is calcined at a temperature of about 350°C for a period of about 4 hours. In other embodiments, the catalyst is calcined at a temperature of up to or about 380°C, 400°C, 500°C or 600°C for a period of about 4 hours.

[0061] In embodiments, calcining comprises (a) increasing to 140°C (from, for example room temperature) at a rate of about 0.5°C/min and dwelling for 4 hours at this temperature; (b) increasing from 140°C to 200°C at a rate of about 0.5°C/min and dwelling for 4 hours at this temperature; (c) increasing from 200°C to 300°C at a rate of about 0.5°C/min and dwelling for 4

hours at this temperature; and (d) decreasing to a temperature of about 70°C at a rate of about 5°C/min, or a any combination of one or more of steps (a)-(d).

[0062] **Catalyst Activation**. Providing iron-based FT catalyst at 100 can further comprise activating the catalyst at 117. Activating can be performed by any method known in the art. For example, in embodiments, activation comprises contacting the spray-dried, calcined or reduced spray-dried catalyst with a gas selected from the group consisting of hydrogen, carbon monoxide, synthesis gas and combinations thereof. The activation gas may comprise synthesis gas having a high molar ratio of hydrogen to carbon monoxide. The high molar ratio of H_2:CO can be a ratio in the range of from about 0.4 to about 4, from about 0.5 to about 2 or from about 0.6 to about 1.5. In embodiments, the high molar ratio is a molar ratio of at least about 0.4, 0.5, 0.6, 2.5, 4, or 10. The catalyst may be calcined or activated by exposure to synthesis gas, hydrogen or carbon monoxide.

[0063] The catalyst can be reduced at 117 by any methods known in the art. The catalyst can be reduced in a fixed bed or a fluidized bed reactor. For example, in embodiments, a spray-dried precipitated catalyst is reduced by contacting the precipitated spray-dried catalyst with a reducing gas selected from the group consisting of hydrogen, carbon monoxide, synthesis gas and combinations thereof at temperature in the range of from about 200°C to about 350°C, from about 250°C to about 300°C, from about 260°C to about 280°C, or a temperature of about 350°C.

[0064] In embodiments, the catalyst is activated prior to protecting. In certain embodiments, the catalyst particles are activated *in situ*. Many different activating procedures for promoted iron Fischer-Tropsch catalysts have been described in the literature. For example, one of the most definitive studies on activating iron Fischer-Tropsch catalysts for use in fixed-bed reactors was published by Pichler and Merkel. (United States Department of Interior Bureau of Mines, Technical Paper 718, By H. Pichler and H. Merkel, Translated by Ruth Brinkley with Preface and Foreword by L. J. E. Hofer, United States Government Printing Office, Washington, D.C., 1949, Chemical and Thermomagnetic Studies on Iron Catalysts For Synthesis of Hydrocarbons). In this study, high activity of the catalyst was correlated with the presence of iron carbides after the activation procedure. The most effective procedure reported utilized carbon monoxide at 325°C at 0.1 atm pressure. The study also showed how the presence of copper and potassium in the catalyst affected activation of the catalyst.

[0065] In embodiments, iron-based FT catalyst is activated by any means known to one of skill in the art. In embodiments, the catalyst is pre-treated in hydrogen. In embodiments, the catalyst is pretreated with a gas comprising carbon monoxide. In some embodiments, the catalyst is activated with substantially 100% CO.

[0066] In embodiments, the catalyst is pre-treated in synthesis gas with a molar ratio of H_2:CO in the range of from about 0.5 to about 5. In embodiments, pre-treatment occurs at preselected conditions of temperature and pressure. In embodiments, these pre-selected conditions of temperature encompass a temperature in the range of from about 250°C to about 300°C. In embodiments, pre-selected conditions of pressure encompass a pressure in the range of from about 1 atm to about 10 atm or from about 5 atm to about 10 atm.

[0067] In embodiments, as described in U.S. Patent No. 5,504,118, the activity and selectivity of the catalyst is improved by subjecting the catalyst particles to a hydrogen-rich synthesis gas at elevated temperature and pressure. The reaction of carbiding of the iron catalyst precursor using a hydrogen-rich synthesis gas and the subsequent Fischer-Tropsch reaction both produce water. Without wishing to be limited by theory, it is believed that the presence of this water prevents super-carburization of the catalyst and thereby improves the activity and selectivity of the catalyst. (See "The Influence of Water and of Alkali Promoter on the Carbon Number Distribution of Fischer-Tropsch Products Formed over Iron Catalysts" by L. Konig *et al.*, Ber. Bunsenges. Phys. Chem. 91, 116-121 (1987)-c VHC Verlagsgesellschaft mbH, D-6940 Weinheim, 1987.)

[0068] In embodiments, hydrogen-rich synthesis gas is used in lieu of an inert gas for maintaining the catalyst in suspension while the slurry is being heated to approximately 200°C. At this point, the synthesis gas is replaced by an inert gas (nitrogen or carbon dioxide) until the activation temperature has been attained at which time activation is carried out using, for example, synthesis gas, hydrogen or carbon monoxide.

[0069] It has been reported in U.S. Patent No. 5,504,118 that the presence of a large amount (20%) by volume of nitrogen in the synthesis gas used for pretreatment of a precipitated unsupported catalyst had no detrimental effect on the activation procedure. In embodiments, activation occurs in the presence of up to about 20% nitrogen.

[0070] In embodiments, the catalyst is activated by contacting the catalyst particles with a mixture of gaseous hydrogen and carbon monoxide at a temperature of from about 250°C to 300°C, for about 0.5 to 5 hours, optionally a water vapor partial pressure of about 1 psia, and a hydrogen to carbon monoxide mol (or volume) ratio in the range of from about 1.3 to 1.5, the activation being effective to increase the selectivity of the activated catalyst in subsequent formation of liquid hydrocarbons in a Fischer-Tropsch reaction. In embodiments, the syngas for activation has a H_2:CO mol ratio of about 1.4. In embodiments, activation in syngas occurs for a time period up to 6 hours.

[0071] In embodiments, activation is effected via a 'typhoon' activation method. In embodiments, such catalyst activation is performed by heating the catalyst to 275°C in nitrogen, feeding syngas at

a H_2:CO ratio of 1.4 once attaining a temperature of 275°C, activating at 275°C under 140 psig pressure for 4-24 hours (depending on the space velocity). Activation may be performed at a space velocity in the range of from about 1 to about 6 nL/h/g cat.

[0072] In embodiments, activation comprises introducing an inert gas into a reactor comprising a slurry of the catalyst at a first temperature; increasing the reactor temperature from the first temperature to a second temperature at a first ramp rate; introducing synthesis gas having a ratio of H_2:CO to the reactor at a space velocity; and increasing the reactor temperature from the second temperature to a third temperature at a second ramp rate. The second temperature may be in the range of from about 150°C to 250°C; alternatively, the second temperature may be about 150°C. The third temperature may be in the range of from about 270°C to 300°C; alternatively, the third temperature may be about 270°C. The reactor pressure may be maintained in the range of from about 0 psig to about 175 psig during activation; alternatively, in the range of from about 30 psig to about 140 psig. The first ramp rate may be in the range of from about 1°C/min to 5°C/min. The second ramp rate may be in the range of from about 0.2°C/min to 1°C/min; alternatively in the range of from about 0.5°C/min to 1°C/min. The space velocity may be in the range of from about 3 to about 4 nl/h/g Fe. The ratio of H_2:CO may be in the range of from about 0.5 to 1.5 during activation.

[0073] In embodiments, an iron Fischer-Tropsch catalyst is activated by introducing an inert gas into a reactor comprising a slurry of the catalyst at a first temperature, increasing the reactor temperature from the first temperature to a second temperature at a first ramp rate, wherein the second temperature is in the range of from about 150°C to 250°C, introducing synthesis gas having a ratio of H_2:CO to the reactor at a space velocity, and increasing the reactor temperature from the second temperature to a third temperature at a second ramp rate, wherein the third temperature is in the range of from about 270°C to 300°C. The reactor pressure may be maintained in the range of from about 0 psig to about 175 psig or in the range of from about 30 psig to about 140 psig during activation. The first ramp rate may be in the range of from about 1°C/min to 5°C/min. The second ramp rate may be in the range of from about 0.2°C/min to 1°C/min. The space velocity may be in the range of from about 3 to about 4 nl/h/g Fe. The ratio of H_2:CO may be in the range of from about 0.5 to 1.5. The second temperature may be about 150°C. The third temperature may be about 270°C.

[0074] In embodiments, activation is performed in synthesis gas at a temperature in the range of from about 150°C to about 270°C for a time period of from about 1 to about 10 hours. The synthesis gas may have a H_2:CO ratio in the range of from about 0.7 to about 1.5, from about 0.7 to

about 1 or from about 0.77 to about 1. The space velocity for activation may be in the range of from about 1 to about 6 nL/h/g cat.

[0075] In embodiments, activation is performed substantially as described in U.S. Patent Number 5,504,118 and/or U.S. Patent Application Number 12/272,960, the disclosures of each of which are hereby incorporated herein for all purposes not contrary to this disclosure.

[0076] The disclosed method further comprises combining the catalyst to be protected with protective material at 200. Desirably, enough protective material is combined with the catalyst to cover the entire surface area of the catalyst. In embodiments, protective material is added to the iron-based FT catalyst at a volumetric ratio of catalyst (i.e. particles) to protective coating (e.g. wax) in the range of from about 0.5 to about 5, from about 1 to about 5, from about 0.5 to about 2 or from about 1 to about 1. In embodiments, protective material is added to the catalyst at a weight ratio of catalyst particles to protective coating (e.g. wax) in the range of from about 0.5 to about 4, from about 0.8 to about 4, from about 0.5 to about 1.5 or from about 1 to about 1.

[0077] The protective material can be selected from the group consisting of waxes. In embodiments, the protective material comprises at least one wax selected from the group consisting poly alpha olefin wax, Fischer-Tropsch wax and combinations thereof. In embodiments, the protective material comprises C18 straight cut. In embodiments, the wax is selected from the group consisting of FT hydrocarbons having a carbon number in the range of from about 10 to about 40, from about 15 to about 30 or from about 15 to about 20. In embodiments, the wax is selected from the group consisting of waxes having a molecular weight in the range of from about 150 to about 600, from about 200 to about 400 or from about 200 to about 300.

[0078] As indicated in Figure 4, which is a block flow diagram of a method 200A of combining a catalyst with protective material according to an embodiment of this disclosure, combining the catalyst with a protective material can comprise slumping a fluidized bed of the catalyst (which may be spray-dried and raw, reduced and/or activated) at 210 and adding a protective material to the slumped bed of catalyst at 220. Combining with protective material at 200/200A produces a catalyst/protective material combination.

[0079] In embodiments, the protective material is combined at 200 or 200A with a precipitated catalyst. In embodiments, the protective material is combined at 200/200A with a precipitated iron-based FT catalyst that has been reduced. In embodiments, the protective material is combined at 200/200A with precipitated spray-dried catalyst that has already been activated. In embodiments, the protective material is combined at 200/200A with a precipitated spray-dried catalyst that has been reduced and subsequently activated at 110 or 110A.

[0080] Shaping 300 comprises forming discrete units from the combination comprising protective material and catalyst. The discrete units can have any size and shape suitable for downstream processing, *i.e.* of a size and shape suitable for transport, for loading into a reactor having certain dimensions of length and width/diameter, for loading into an activation reactor having certain dimensions (*e.g.* when the catalyst is not activated prior to protecting), etc.

[0081] Shaping at 300 may be performed as known in the art. As indicated in Figure 5, which is a block flow diagram of a method of shaping 300A according to an embodiment of this disclosure, shaping can comprise removing the catalyst/coating combination from the coating reactor at 310 and passing the combination through a shaping apparatus configured to form discrete units of protected catalyst at 320. The shaping apparatus can be any apparatus known in the art to be suitable for forming discrete units of catalyst from a wax/catalyst combination. The shaping apparatus can comprise apparatus configured for shaping the protective material-coated catalyst (*e.g.* wax-coated catalyst) into pellets, *i.e.* the method can comprise pelletizing the coated catalyst. The discrete units may be roughly or substantially spherical, oblong, tabletted or other shape suitable for transportation and loading to a reactor (*e.g.* a production reactor or an activation reactor, as discussed further hereinbelow). The shaping apparatus can be positioned, for example, on an outlet line of the coating reactor whereby catalyst is shaped as it exits the coating reactor.

[0082] In embodiments, the catalyst is not activated prior to protecting it with protective material. In such embodiments, the method can further comprise reducing and/or activating the catalyst subsequent to shaping the catalyst. Activation can be performed via the methods described hereinabove. Protected non-pre-activated catalyst can be transferred to a production reactor and activated *in situ* prior to start-up or the protected catalyst can be transferred to an activation reactor and activated prior to introduction of the activated catalyst into a production reactor. In embodiments, the protected catalyst is first heated to a temperature (e.g. above 275°C in some embodiments) at which the protective material (i.e. wax) melts in N_2 and then activation gas (e.g. syngas) is introduced for activation.

[0083] In embodiments, protected catalyst optionally comprising support material (e.g. $MgAl_2O_4$, $MgAl_2O_4$-SiO_2, Al_2O_3, SiO_2, SiO_2-Al_2O_3, TiO_2, etc.) is first heated to 200°C in N_2, and then syngas is fed, and the temperature is ramped to a temperature in the range of about 285°C to 300°C. In embodiments, the syngas used for activation has a H_2:CO ratio in the range of from about 0.7 to about 1.5. In embodiments, the activating synthesis gas has a H_2:CO ratio of about 0.7. In embodiments, the temperature is ramped from 200°C to a temperature of from about 285°C to about 300°C at a ramp rate in the range of from 1°C/min to about 5°C/min.

[0084] Description of a method according to an embodiment of this disclosure will now be made with reference to Figure 6, which is a schematic of an apparatus 400 suitable for use in providing protected catalyst according to an embodiment of this disclosure. It is to be understood that reactors A, B, C and D depicted in I, II, III and IV can be provided by a single reactor, or by two, three or four distinct reactors. For example, reactors A and B shown in stages I and II can be the same (*i.e.* a single) reactor, reactors C and D shown in stages III and IV can be the same reactor (*i.e.* a single) reactor, or all reactors A-D can be a single reactor.

[0085] At 115A, an amount of catalyst particles is fluidized in a fluidization reactor A to form fluidized catalyst bed 1. For example, as discussed hereinabove, a volume of catalyst can be fluidized with inert gas (*e.g.* nitrogen), which may be introduced into reactor A via a valve V2. Any excess gas and/or vapor (*e.g.* water vapor) may exit reactor A via an outlet gas line and valve V3. The fluidized catalyst may be heated to a suitable reduction temperature for the selected catalyst. In embodiments, the reduction temperature is in the range of from about 200°C to about 350°C, from about 250°C to about 300°C or from about 260°C to about 280°C. At 117A, the fluidized catalyst can be reduced and/or activated as known in the art, for example, by the introduction of reducing gas and subsequently activating gas via valve V2. Reducing may be provided by cutting in reducing gas (*i.e.* ceasing introduction of fluidizing gas such as nitrogen and introducing reducing gas such as hydrogen, carbon monoxide or synthesis gas) and reducing the fluidized bed of catalyst for a reduction time in the range of from about 4 hours to about 48 hours, from about 6 hours to about 24 hours, or from about 8 hours to about 12 hours.

[0086] The fluidized, spray-dried reduced catalyst may subsequently be carbided (*i.e.* activated) by contact of the fluidized bed of catalyst 2 with an activation gas. Activation can be performed as known in the art, for example, via the methods described hereinabove. For example, as indicated at stage II, activation gas can be introduced into a reactor B via valve V2. As discussed hereinabove, the activation gas may be selected from the group consisting of hydrogen, carbon monoxide, synthesis gas and combinations thereof. The activation gas may comprise a synthesis gas having a high molar ratio of hydrogen to carbon monoxide. Such a high ratio of hydrogen to carbon monoxide may be a ratio in the range of from about 0.5 to about 2.5, from about 0.6 to about 2, or from about 0.7 to about 1.5. Activating can comprise switching from a reducing gas to an activating gas, such as synthesis gas with a suitable molar ratio of H_2:CO, and activating for a time period in the range of from about 4 hours to about 48 hours, from about 6 hours to about 24 hours, or from about 8 hours to about 12 hours and a temperature in the range of from about 200°C to about 350°C, from about 250°C to about 300°C or from about 260°C to about 280°C to activate the catalyst.

[0087] Activation may take place in the same or different fixed or fluidized bed reactor from reducing. As indicated in Figure 6, the reduced and/or activated catalyst may then, under an inert atmosphere (or carbiding atmosphere), be transferred to a wax coating vessel C, or may be combined with wax in the same vessel (A or B). The fluidized bed may or may not be slumped (*i.e.* the rate of introduction of fluidization gas to the coating vessel reduced, aborted or absent) prior to the addition of the protective material thereto. In embodiments, the fluidized bed is slumped by reducing the fluidization gas space velocity in the range of from about 0.5 to about 10 NLPH (normal liters per hour, normalized at a temperature of 0°C and a pressure of 1 atm) per gram catalyst to a decreased or 'slumped' flow rate in the range of from about 2 to about 4 NLPH per gram catalyst. In embodiments, a trickle flow of fluidization gas is provided via fluidization nozzles during combining at 200/200A.

[0088] Combining the catalyst particles with protective material 200/200A can comprise slumping the fluidized bed of catalyst at 210 to provide a slumped bed and adding protective material to the slumped bed 3 at 220. In embodiments in which an air-sensitive catalyst is to be protected, combining comprises adding an amount of protective material effective to cover all of the air sensitive catalyst. In embodiments, adding protective material to the bed comprises introducing a molten form of the protective material (*e.g.* molten wax) into the vessel whereby the molten material coats the slumped bed 3 of catalyst. In embodiments, adding protective material to the bed comprises adding a solid form of the protective material to the bed (*e.g.* solid wax) and heating whereby the solid material melts and coats the catalyst therein. Protective material may be introduced into the coating reactor C via a protective material inlet line and valve V1. Fluidization of the bed during protective material addition may be provided by the introduction of fluidization gas via valve V2.

[0089] Following the addition of protective material to the catalyst bed, the catalyst/protective material combination is shaped at 300/300A. As indicated in stage IV of Figure 6, the combination of catalyst and protective material is removed from reactor D (which is desirably the same reactor as reactor C). Inert gas may be introduced into the top of the reactor during stage IV, *i.e.* via a line and valve V3 to help remove (*e.g.* to help 'push') the protected catalyst from the reactor through an outlet line and valve V4. In embodiments, catalyst/protective material combination is removed from the reactor via gravity. The catalyst/protective material combination passes through catalyst shaping apparatus 6 which produces shaped catalyst units 5. Shaping can comprise draining a molten wax-covered catalyst from the coating reactor, shaping the drained or draining material and cooling into a stable state for transportation and/or transferring and/or loading into a reactor.

[0090] A protected (*i.e.* coated) activated product can be shaped as desired to assist in loading a synthesis reactor (*i.e.* a Fischer-Tropsch reactor). In applications, the protected catalyst is formed into small spheres or otherwise pelletized. Such pelletization may significantly shorten the time needed to get a production reactor (*e.g.* an FT synthesis reactor) on-line, by enabling more convenient handling of the protected, shaped catalyst. The process may also increase the stability of operation during catalyst replacement and/or addition of make-up catalyst to a production reactor.

[0091] In embodiments, the method comprises providing catalyst particles that are precipitated and optionally reduced, but not activated at 100, combining the catalyst particles with protective material at 200, and shaping the coated catalyst at 300. In such embodiments, shaped catalyst is coated with protective material prior to activation. In such applications, the shaped unactivated catalyst may be introduced into a reduction and/or activation reactor wherein the catalyst is reduced and/or activated prior to introduction into a synthesis reactor or may be introduced directly into a synthesis reactor for activation *in situ*. In such applications, the protective material is melted from the catalyst and activation carried out as described hereinabove. Thus, as described, catalyst activation may be performed prior to or after protectively coating. Desirably, reduction (*e.g.* reduction by contact with hydrogen gas) followed by synthesis gas precarbiding/activation is utilized to ensure that the catalyst is in a more stable form (*i.e.* more oxygen resistant) to be protectively coated.

[0092] ***Method of Producing FT Hydrocarbons***. In embodiments, the method of providing protected catalyst further comprises producing a product catalyzed by the catalyst. In such embodiments, the method further comprises removing the protective layer. In instances in which the catalyst is activated prior to coating with protective material, producing a product with the protected pre-activated catalyst can comprise introducing the protected catalyst into a production reactor, heating to a melting temperature at which the protective material melts, removing the protective material from the reactor and operating the reactor under conditions suitable to produce the desired product. For example, producing product via the protected catalyst can comprise introducing the protected pre-activated catalyst into an FT reactor, heating to a temperature above the temperature at which the protective material melts, removing the protective material from the reactor, and introducing synthesis gas into the reactor under conditions of temperature and pressure suitable for the production of FT hydrocarbons. Depending on the protective material with which the catalyst is protected, the melting temperature can be a temperature in the range of from about 60°C to about 200°C, from about 70°C to about 150°C or from about 80°C to about 120°C.

[0093] In embodiments, the catalyst is not activated prior to coating with protective material. In such embodiments, the method can further comprise introducing protected catalyst directly into an FT reactor prior to or during start-up, increasing the temperature to a melting temperature selected from temperatures above which the protective material melts (desirably at or near the melting temperature of the protective material, *i.e.* not excessively high), draining the melted protective material from the FT reactor, and subsequently introducing synthesis gas to the reactor as known in the art, under conditions of temperature and pressure at which FT hydrocarbons are synthesized.

[0094] Alternatively or additionally, in embodiments in which non-preactivated protected catalyst is utilized, the method can further comprise introducing the protected catalyst into an activation reactor, increasing the temperature to a melting temperature selected from temperatures above which the protective material melts (desirably at or near the melting temperature of the protective material, *i.e.* not excessively high), draining the melted protective material from the activation reactor, and subsequently introducing the catalyst to an FT production reactor as known in the art, and operating the production FT reactor under conditions of temperature and pressure at which FT hydrocarbons are synthesized.

[0095] In embodiments, it is envisaged that the above methods can be combined and/or both protected pre-activated catalyst and protected non-preactivated catalyst may both be utilized. For example, protected preactivated catalyst may be introduced directly into an FT reactor during start-up, as described hereinabove, and protected non-preactivated catalyst or protected preactivated catalyst utilized to provide replacement catalyst during FT production. For example, protected non-preactivated catalyst can be activated in an activation reactor and added to an FT production reactor as needed for replacement catalyst. Alternatively or additionally, protected activated catalyst can be introduced into a preheating reactor heated to a temperature above the melting temperature of the protective material, the protective material drained from the preheating reactor, and the activated non-coated catalyst subsequently introduced into the production FT reactor as needed as make-up and/or replacement catalyst.

[0096] The method of producing FT hydrocarbons can further comprise introducing a feed gas comprising synthesis gas (*i.e.* carbon monoxide and hydrogen) into an FT production reactor that has been loaded with slurry phase catalyst via any of the above-disclosed methods. The feed gas comprises a mixture of H_2 and CO. This mixture may be referred to as synthesis gas or syngas. In embodiments, the molar ratio of H_2 to CO is in the range of from about 0. 5 to about 10, from about 0.75 to about 5, from about 0.75 to about 3, from about 1 to about 3, from about 1.5 to about 3, from about 1.8 to about 2.5, from about 1.9 to about 2.2 or from about 2.05 to about 2.10. In embodiments, at least a portion of the feed gas comprises synthesis gas produced via

partial oxidation, reforming of CO_2, steam reforming, autothermal reforming, gasification (*e.g.* coal gasification), or a combination thereof. In embodiments, at least a portion of the feed gas comprises synthesis gas produced via steam reforming. Such synthesis gas from steam reforming may have a mole ratio of H_2 to CO of about 3. In embodiments, at least a portion of the feed gas comprises synthesis gas produced via partial oxidation. Such synthesis gas from partial oxidation may have a mole ratio of H_2 to CO of about 2. In embodiments, at least a portion of the feed gas comprises synthesis gas produced via autothermal reforming. Such synthesis gas from autothermal reforming may have a mole ratio of H_2 to CO of about 2.5. In embodiments, at least a portion of the feed gas comprises synthesis gas produced via reforming of CO_2. Such synthesis gas from reforming of CO_2 may have a mole ratio of H_2 to CO of about 1. In embodiments, at least a portion of the feed gas comprises synthesis gas produced via gasification. In embodiments, at least a portion of the feed gas comprises synthesis gas produced via gasification of coal. Such synthesis gas from (*e.g.* coal) gasification may have a mole ratio of H_2 to CO of about 1.

[0097] The feed gas may further comprise other components, including but not limited to CO_2 and/or H_2O, light hydrocarbons having from one to about four carbon atoms or having one or two carbon atoms. In embodiments, the feed gas comprises from about 30 to about 95 volume percent CO, from about 40 to about 75 volume percent CO or from about 50 to about 60 volume percent CO. In embodiments, the feed gas comprises from about 55 to about 95 volume percent H_2, from about 70 to about 95 volume percent H_2, or from about 80 to about 95 volume percent H_2. In embodiments, the feed gas further comprises, in addition to carbon monoxide and hydrogen (*i.e.* in addition to synthesis gas) from about 0 to about 40 volume percent CO_2, from about 0 to about 30 volume percent CO_2 or from about 0 to about 20 volume percent CO_2. The feed gas may further comprise from about 0 to about 80 volume percent light hydrocarbons, from about 1 to about 80 volume percent light hydrocarbons, or from about 1 to about 50 volume percent light hydrocarbons.

[0098] ***Features/Advantages.*** Via the disclosed method, catalyst activation, *i.e.* carbiding, can be completed at a catalyst manufacturing site, providing simplification of startup of a fresh reactor batch at a production site. A further, and possibly more significant, advantage is evident during on-line catalyst removal and replacement. Via embodiments of the disclosed method, activated catalyst is readily available for loading into a production reactor, reducing reaction equipment (*i.e.* no dedicated activation vessels are required) and/or process time (*e.g.* no time lost for catalyst activation). According to embodiments, the surrounding protective coating can be melted from protected pre-activated catalyst particles and the activated catalyst introduced directly into a

production reactor (*e.g.* an FT synthesis reactor), or the surrounding protective material can be melted *in situ* in a production reactor.

[0099] The disclosed method of protecting a catalyst facilitates transport and/or handling of the catalyst prior to introduction of the catalyst into a reactor in which it will be utilized to catalyze a reaction and/or helps to maintain reduction and/or activity of the catalyst.

[00100] The protected catalyst of this disclosure comprises discrete units of catalyst coated with a protective material. The protective material may form an outer coating having a thickness in the range of from about 1 mm to about 10 mm, from about 1 mm to about 5 mm or from about 1 mm to about 2 mm. Desirably, the protective method does not negatively affect catalyst properties, including, but not limited to, catalyst activity, catalyst selectivity and catalyst lifetime.

EXAMPLE

[00101] The following example is presented to further illustrate the present invention and is not to be construed as unduly limiting the scope of this invention.

[00102] Iron FT catalyst was activated via CO fixed-bed activation at a temperature of 270°C, a pressure of 175 psig and a carbon monoxide space velocity of 2nL/h/gFe. The temperature was ramped to 270°C at a ramping rate of 1°C/min and held at 270°C for a time of 24 hours. The activation was performed using 70%CO and 30% N_2. Subsequent activation, the catalyst was covered with wax.

[00103] While preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (*e.g.* from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, and so forth). Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, and the like.

[00104] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the

present invention. Thus, the claims are a further description and are an addition to the preferred embodiments of the present invention. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A method of providing a protected Fischer-Tropsch catalyst, the method comprising:

providing catalyst particles functional for catalyzing the Fischer-Tropsch synthesis reaction;

combining the catalyst particles with a protective material such that the catalyst particles are coated with the protective material; and

shaping the combination comprising catalyst and protective material to provide the protected catalyst.

2. The method of claim 1 wherein the catalyst is a spray-dried catalyst.

3. The method of claim 2 wherein the spray-dried catalyst is a precipitated iron-based catalyst.

4. The method of claim 1 further comprising introducing the protected catalyst into a reactor.

5. The method of claim 4 wherein the reactor is a Fischer-Tropsch synthesis reactor.

6. The method of claim 1 further comprising fluidizing the catalyst particles, to provide a fluidized bed.

7. The method of claim 6 wherein fluidizing comprises introducing an inert gas into a vessel containing the catalyst particles.

8. The method of claim 6 further comprising reducing the catalyst particles.

9. The method of claim 8 wherein reducing comprises contacting the fluidized catalyst particles with reducing gas at a reduction temperature.

10. The method of claim 9 wherein the reducing gas comprises at least one component selected from the group consisting of hydrogen, carbon monoxide and synthesis gas.

11. The method of claim 9 wherein contacting the fluidized catalyst particles with reducing gas is performed at a reducing temperature in the range of from about 200°C to about 350°C for a time in the range of from about 4 hours to about 48 hours.

12. The method of claim 8 further comprising contacting the catalyst particles with activation gas under activation conditions, whereby the catalyst particles are carbided.

13. The method of claim 12 further comprising slumping the fluidized bed prior to combining the catalyst particles with protective material.

14. The method of claim 1 further comprising activating the catalyst by contacting the catalyst with activation gas.

15. The method of claim 14 wherein activating is performed prior to combining the catalyst particles with protective material.

16. The method of claim 14 wherein activating is performed subsequent to shaping.

17. The method of claim 16 wherein activating further comprises introducing the protected catalyst into an activation reactor, melting the protective material, and contacting the catalyst with an activation gas.

18. The method of claim 17 wherein the activation reactor is a dedicated activation reactor.

19. The method of claim 17 wherein the activation reactor is the production reactor.

20. The method of claim 14 wherein the activation gas is selected from the group consisting of synthesis gas, carbon monoxide, hydrogen and combinations thereof.

21. The method of claim 1 wherein shaping the catalyst to provide protected catalyst comprises shaping the coated catalyst into shapes selected from substantially spherical, oblong, tabletted, cylindrical, and combinations thereof.

22. The method of claim 1 wherein the catalyst particles have an average size of less than about 150μm.

23. The method of claim 1 wherein the protective material comprises wax.

24. The method of claim 23 wherein the wax is selected from the group consisting of poly alpha olefin waxes and Fischer-Tropsch waxes.

25. The method of claim 24 wherein the protective coating comprises FT wax.

26. The protected catalyst of claim 1.

27. A method for providing protected Fischer-Tropsch catalyst, the method comprising:

fluidizing a bed of catalyst particles having FT functionality;

reducing the catalyst particles by contacting the catalyst particles with reducing gas under reducing conditions;

activating the reduced catalyst particles by contacting the reduced catalyst particles with an activation gas under activation conditions;

combining the activated catalyst, under inert or carbiding atmosphere, with molten wax, whereby the catalyst particles are coated with wax; and

shaping the wax-coated catalyst particles to provide the protected catalyst.

28. The method of claim 27 further comprising introducing the shaped wax-coated catalyst into a reactor.

29. The method of claim 28 further comprising melting the wax from the shaped wax-coated catalyst in the reactor to provide a catalyst slurry and introducing the catalyst slurry into a production reactor.

30. The method of claim 28 further wherein the reactor is a production reactor.

31. The method of claim 30 further comprising operating the production reactor at a temperature above that at which the wax melts.

32. The method of claim 28 wherein the production reactor is an FT synthesis reactor.

33. The protected catalyst of claim 27.

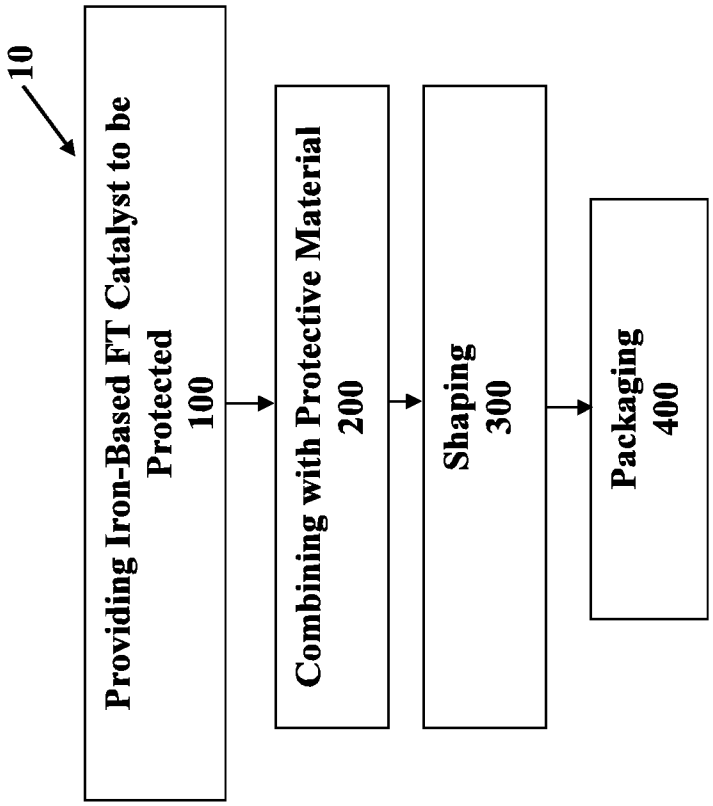
10
Providing Iron-Based FT Catalyst to be Protected
100
Combining with Protective Material
200
Shaping
300
Packaging
400

FIG. 1

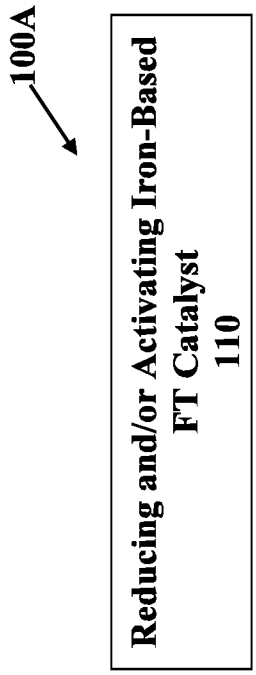
100A
Reducing and/or Activating Iron-Based FT Catalyst
110

FIG. 2

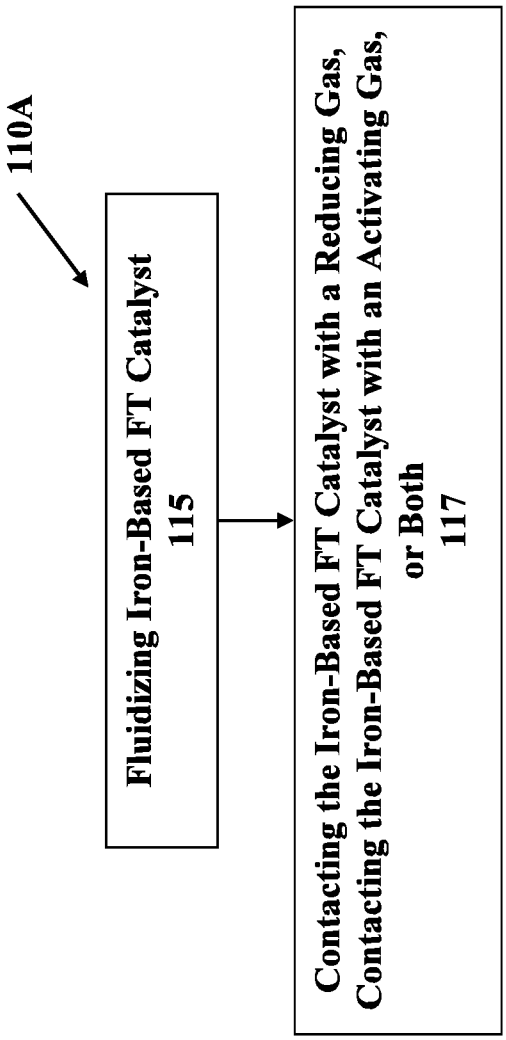
110A
Fluidizing Iron-Based FT Catalyst
115
Contacting the Iron-Based FT Catalyst with a Reducing Gas, Contacting the Iron-Based FT Catalyst with an Activating Gas, or Both
117

FIG. 3

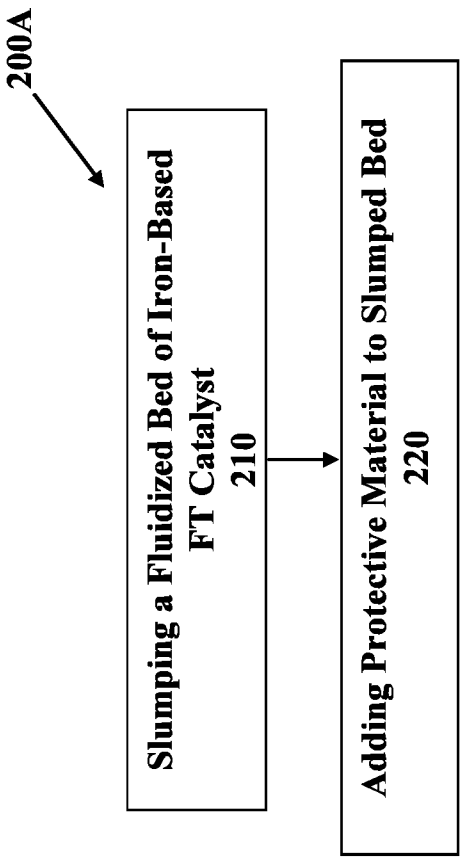
200A
Slumping a Fluidized Bed of Iron-Based FT Catalyst
210
Adding Protective Material to Slumped Bed
220

FIG. 4

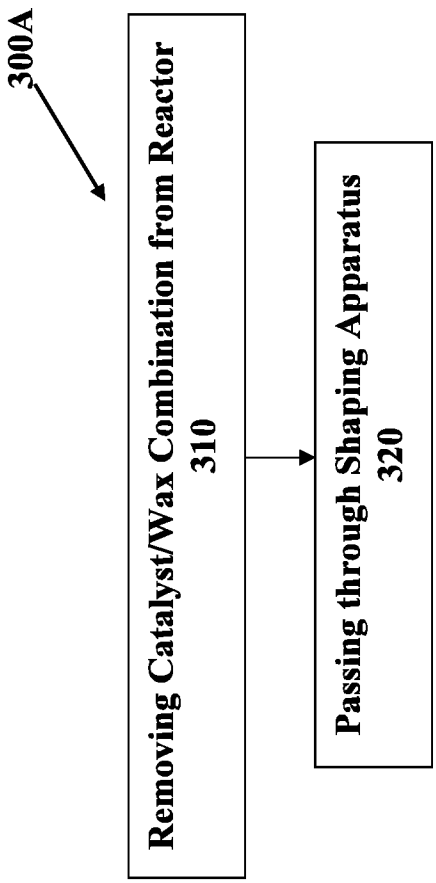
300A
Removing Catalyst/Wax Combination from Reactor
310
Passing through Shaping Apparatus
320

FIG. 5

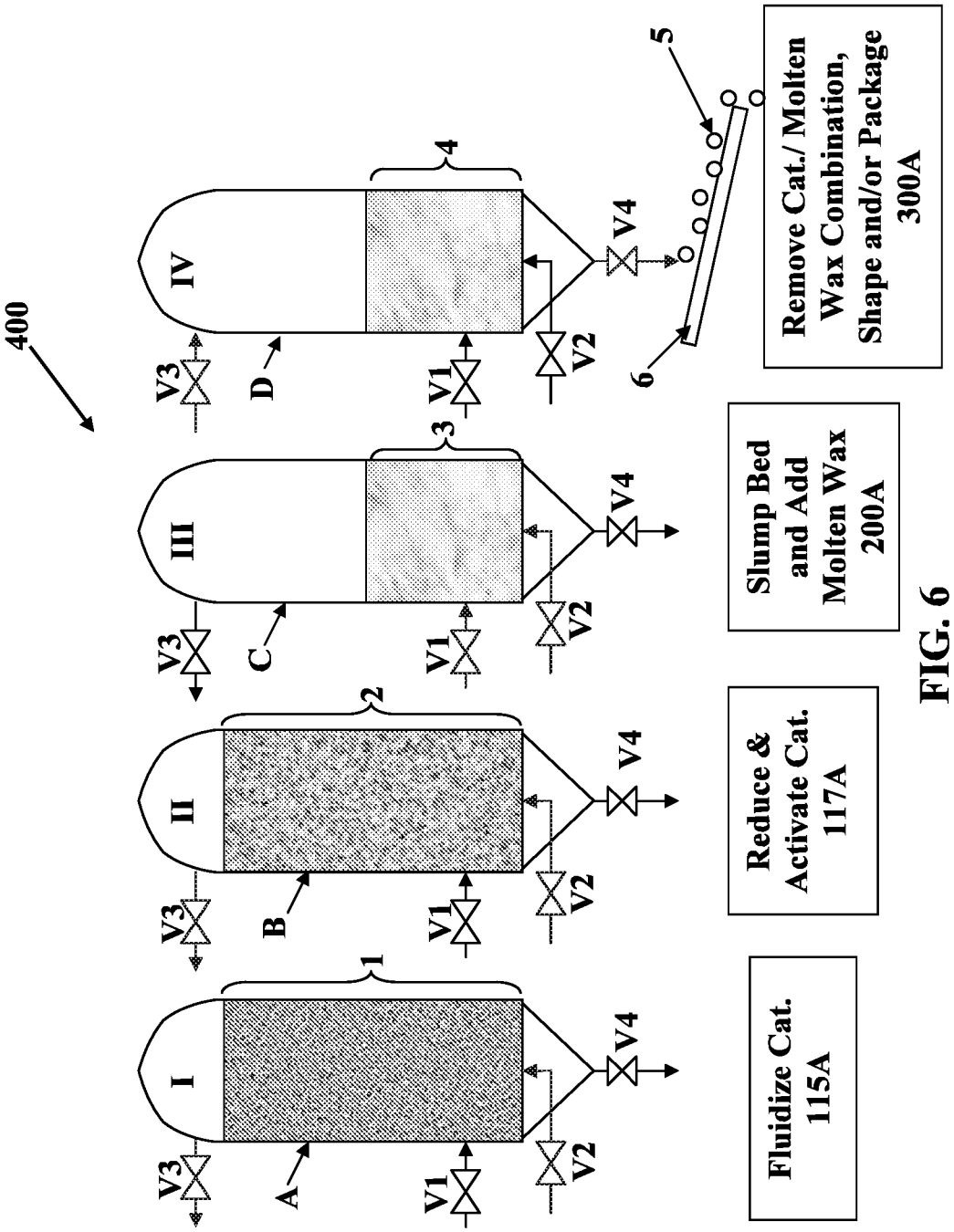
400
I
II
III
IV
V1
V2
V3
V4
A
B
C
D
1
2
3
4
5
6
Fluidize Cat. 115A
Reduce & Activate Cat. 117A
Slump Bed and Add Molten Wax 200A
Remove Cat./ Molten Wax Combination, Shape and/or Package 300A

FIG. 6