

SELECTIVE HYDROGENATION CATALYST CONTAINING BIMODAL SUPPORT AND METHODS OF MAKING AND USING SAME

BACKGROUND

Technical Field

[0001] The present disclosure relates to the production of unsaturated hydrocarbons, and more particularly to a selective hydrogenation catalyst and methods of making and using same.

Background

[0002] Unsaturated hydrocarbons such as ethylene and propylene are often employed as feedstocks in preparing value added chemicals and polymers. Unsaturated hydrocarbons can be produced by pyrolysis or steam cracking of hydrocarbons including hydrocarbons derived from coal, hydrocarbons derived from synthetic crude, naphthas, refinery gases, ethane, propane, butane, and the like. Unsaturated hydrocarbons produced in these manners usually contain small proportions of highly unsaturated hydrocarbons such as acetylenes and diolefins that can adversely affect the production of subsequent chemicals and polymers. Thus, to form an unsaturated hydrocarbon product such as a polymer grade monoolefin, the amount of acetylenes and diolefins in the monoolefin stream is typically reduced. For example, in polymer grade ethylene, the acetylene content typically is less than about 2 ppm.

[0003] One technique commonly used to reduce the amount of acetylenes and diolefins in an unsaturated hydrocarbon stream primarily comprising monoolefins involves selectively hydrogenating the acetylenes and diolefins to monoolefins. This process is selective in that hydrogenation of the monoolefin and the highly unsaturated hydrocarbons to saturated hydrocarbons is minimized. For example, the hydrogenation of ethylene or acetylene to ethane is minimized. An ongoing need exists for improved selective hydrogenation catalysts.

SUMMARY

[0004] Disclosed herein is a composition comprising a support formed from a high surface area alumina and having a low angularity particle shape; and at least one catalytically active metal, wherein the support has pores, a total pore volume, and a pore size distribution; wherein the pore size distribution displays at least two peaks of pore diameters, each peak having a maximum; wherein a first peak has a first maximum of pore diameters of equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters of less than about 200 nm; and

wherein greater than or equal to about 5% of a total pore volume of the support is contained within the first peak of pore diameters.

[0005] Also disclosed herein is a method of preparing a hydrogenation catalyst comprising shaping a mixture comprising a high surface area alumina, a pore former, and water to form a shaped support, wherein the shaped support comprises a low angularity particle shape; drying the shaped support to form a dried support; calcining the dried support to form a calcined support; contacting the calcined support with a chlorine-containing compound to form a chlorided support; reducing the amount of chloride in the chlorided support to form a cleaned support; and contacting the cleaned support with a Group 10 metal and a Group 1B metal to form a hydrogenation catalyst, wherein a pore size distribution for the hydrogenation catalyst displays at least two peaks of pore diameters, each peak having a maximum, wherein a first peak has a first maximum of pore diameters that is equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters that is less than about 200 nm.

[0006] Also disclosed herein is a low angularity particle shape support formed from a high surface area alumina, wherein a pore size distribution for the low angularity particle shape support displays at least two peaks of pore diameters, each peak having a maximum; wherein a first peak has a first maximum of pore diameters of equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters of less than about 200 nm; wherein greater than or equal to about 15% of a total pore volume of the low angularity particle shape support is contained within the first peak of pore diameters; and wherein the low angularity particle shape support is a sphere or a refined extrudate and has an attrition of from about 0.05% to about 5%.

[0007] Also disclosed herein is a method of preparing a hydrogenation catalyst comprising: selecting an inorganic material having a multimodal distribution of pore diameters, wherein at least one distribution of pore diameters comprises pores having a diameter of equal to or greater than about 200 nm; shaping a mixture comprising the inorganic material and water to form a shaped support wherein the shaped support has a low angularity particle shape and an attrition of from about 0.05% to about 5%; drying the shaped support to form a dried support; calcining the dried support to form a calcined support; and contacting the calcined support with a Group VIII metal and a Group 1B metal to form a hydrogenation catalyst.

[0008] Also disclosed herein is a method comprising preparing a plurality of low angularity particle shaped supports consisting essentially of α -alumina formed from a high surface area

alumina, wherein the low angularity shaped supports have an attrition of from about 0.05% to about 5%; plotting the pore diameter as a function of a log of differential mercury intrusion for the low angularity particle shaped supports; and identifying the low angularity particle shaped supports having at least two peaks, each peak having a maximum, wherein a first peak comprises pores with a first pore diameter maximum equal to or greater than about 200 nm, and wherein the first peak of pore diameters represents greater than or equal to about 5% of a total pore volume of the low angularity particle shaped supports.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] For a more complete understanding of the present disclosure and the advantages thereof, reference is now made to the following brief description, taken in connection with the accompanying drawings and detailed description, wherein like reference numerals represent like parts.

[0010] Figure 1 depicts a process flow diagram of an embodiment of a selective hydrogenation process.

[0011] Figures 2-6 are plots of the log of differential mercury intrusion as a function of pore size diameter for the samples from Example 1.

[0012] Figure 7 is a plot of the temperature necessary to maintain a 90% conversion of acetylene as a function of time for the samples from Example 1.

[0013] Figure 8 is a plot of the ethylene selectivity as a function of time for the samples from Example 1.

[0014] Figure 9 is a plot of the incremental and cumulative differential mercury intrusion as a function of pore size diameter for the samples from Example 3.

DETAILED DESCRIPTION

[0015] It should be understood at the outset that although an illustrative implementation of one or more embodiments are provided below, the disclosed systems and/or methods can be implemented using any number of techniques, whether currently known or in existence. The disclosure should in no way be limited to the illustrative implementations, drawings, and techniques illustrated below, including the exemplary designs and implementations illustrated and described herein, but can be modified within the scope of the appended claims along with their full scope of equivalents.

[0016] Disclosed herein are hydrogenation catalysts comprising a Group 10 metal and a catalyst support. In an embodiment the catalyst support is an inorganic catalyst support having a characteristic pore size distribution. In an embodiment, the catalyst support comprises an oxide of a metal or metalloid and displays a characteristic pore size distribution. Catalysts of the type disclosed herein can display a hydrogenation selectivity that remains stable over a longer time period as will be described in more detail later herein. Also disclosed herein is a method of preparing a hydrogenation catalyst comprising shaping a mixture comprising a high surface area alumina (e.g., activated alumina and/or gamma alumina), a pore former, and water to form a shaped support; drying the shaped support to form a dried support; calcining the dried support to form a calcined support; contacting the calcined support with a chlorine-containing compound to form a chlorided support; reducing the amount of chloride in the chlorided support to form a cleaned support; and contacting the cleaned support with a Group 10 metal and a Group 1B metal to form a hydrogenation catalyst, wherein the calcined support, the chlorided support, the cleaned support, and/or the hydrogenation catalyst displays a characteristic pore size distribution and has a low angularity particle shape (LAPS).

[0017] In an embodiment, the catalyst comprises an inorganic catalyst support. In an embodiment, the catalyst comprises a support of an oxide of a metal or metalloid. In an embodiment, the catalyst support comprises silica, titania, alumina, aluminate, or combinations thereof. Alternatively, the catalyst support consists or consists essentially of silica, titania, alumina, aluminate, or combinations thereof. In an embodiment, the catalyst support comprises a spinel. Alternatively, the catalyst support consists or consists essentially of a spinel. Herein, a spinel refers to any of a class of minerals of general formulation $A^{2+}B_2^{3+}O_4^{2-}$ which crystallize in the cubic (isometric) crystal system, with the oxide anions arranged in a cubic, close-packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. Nonlimiting examples of materials suitable for use in the catalyst supports of this disclosure include aluminas, silicas, titanias, zirconias, aluminosilicates (e.g., clays, ceramics, and/or zeolites), spinels (e.g., zinc aluminate, zinc titanate, and/or magnesium aluminate), or combinations thereof.

[0018] In an embodiment, the catalyst support comprises an alumina. Alternatively the catalyst support consists or consists essentially of an alumina. For example, the catalyst support can comprise, consist of, or consist essentially of an alpha (α)-alumina support. The α -alumina

support can be prepared using any suitable methodology. The alumina support can include additional components that do not adversely affect the catalyst such as zirconia, silica, thoria, magnesia, fluoride, sulfate, phosphate, titania, alkali metals, or mixtures thereof.

[0019] The catalyst support can have a surface area of from about 1 square meters per gram (m^2/g), to about 35 m^2/g , or alternatively of from about 3 m^2/g to about 25 m^2/g , or alternatively of from about 5 m^2/g to about 15 m^2/g . The surface area of the support can be determined using any suitable method. An example of a suitable method for determining the surface area of the support includes the Brunauer, Emmett, and Teller ("BET") method, which measures the quantity of nitrogen adsorbed on the support.

[0020] In an embodiment, a catalyst support of the type disclosed herein is further characterized by a total pore volume as measured by differential mercury intrusion in the range of from about 0.1 cc/g to about 0.9 cc/g, alternatively from about 0.1 cc/g to about 0.6 cc/g, alternatively from about 0.2 cc/g to about 0.55 cc/g, alternatively from about 0.2 cc/g to about 0.8 cc/g, or alternatively from about 0.3 cc/g to about 0.7 cc/g. The pore volume of the support can be measured by a mercury intrusion method such as is described in ASTM UOP578-02, entitled "Automated Pore Volume and Pore Size Distribution of Porous Substances by Mercury Porosimetry," which is incorporated herein by reference in its entirety.

[0021] In an embodiment the catalyst support, the resultant catalyst, or both of the type disclosed herein displays a plot of the pore diameter on a logarithmic base 10 axis versus a logarithmic base 10 of differential mercury intrusion having two to four peaks corresponding to the presence of at least two to four distributions of pore diameters. Hereinafter, a plot of the pore diameter on a logarithmic base 10 axis as a function of a logarithmic base 10 of differential mercury intrusion is referred to as the pore size distribution.

[0022] In an embodiment, a catalyst support, the resultant catalyst, or both of the type disclosed herein is further characterized by an at least bimodal pore size distribution. In an embodiment a catalyst support, the resultant catalyst, or both of the type disclosed herein displays a pore size distribution having at least two peaks corresponding to the presence of at least two distributions of pore diameters. The first peak, designated peak A, corresponds to distribution A and can have a first maximum of pore diameters equal to or greater than about 120 nm. For example, peak A can have a maximum of pore diameters of from about 200 nm to about 9000 nm,

alternatively from about 400 nm to about 8000 nm, or alternatively from about 600 nm to about 6000nm.

[0023] The second peak, designated peak B, corresponds to distribution B and can have a second maximum of pore diameters of less than about 120 nm, , alternatively less than about 130 nm, alternatively less than about 150 nm, alternatively less than about 200 nm. For example, peak B can have a maximum of pore diameters of from about 15 nm to less than about 190 nm, alternatively from about 15 nm to less than about 130 nm, alternatively from about 15 nm to less than about 120 nm, alternatively from about 25 nm to about 115 nm, alternatively from about 50 nm to about 115 nm, alternatively from about 25 nm to about 170 nm, or alternatively from about 30 nm to about 150 nm. Examples of peak A and peak B are identified in Figures 3, 4, 5, 6, and 9.

[0024] In an embodiment, the distance between the maximum of peak A and the maximum of peak B is at least about 400 nm, alternatively at least 500 nm, alternatively at least about 500 nm alternatively from about 400 nm to about 3900 nm, or alternatively from about 400 nm to about 2900 nm. Pore diameter distributions can be Gaussian or Non-Gaussian. In an embodiment peak A, peak B, or both is non-Gaussian. In an embodiment, peak A is non-Gaussian and displays a peak width at half height that is greater than the peak width at half height of peak B.

[0025] In an embodiment greater than or equal to about 5% of the total pore volume of the catalyst support, the resultant catalyst, or both is contained within peak A, alternatively greater than or equal to about 10% of the total pore volume of the catalyst support is contained within peak A, or alternatively greater than or equal to about 15% of the total pore volume of the catalyst support is contained within peak A. In an embodiment from about 5% to about 75% of the total pore volume of the catalyst support, the resultant catalyst, or both is contained within peak A, alternatively from about 10% to about 60% of the total pore volume of the catalyst support is contained within peak A, or alternatively from about 15% to about 40% of the total pore volume of the catalyst support is contained within peak A. In an embodiment less than or equal to about 95% of the total pore volume of the catalyst support, the resultant catalyst, or both is contained within peak B, alternatively less than or equal to about 90%, alternatively less than or equal to about 85%. In an embodiment from about 95% to about 25% of the total pore volume of the catalyst support, the resultant catalyst, or both is contained within peak B, alternatively from about 90% to about 40% of the total pore volume of the catalyst support is contained within peak B, or alternatively

from about 85% to about 60% of the total pore volume of the catalyst support is contained within peak B.

[0026] In an embodiment, a catalyst support of the type disclosed herein is formed from a mixture comprising an oxide of a metal or metalloid, a pore former, and water which are contacted and formed into a shaped support (e.g., an extrudate). Herein a pore former (also known as a pore generator) refers to any compound that can be mixed with the above components and that is combustible upon heating thereby producing voids. The pore former helps to maintain and/or increase the porosity of the catalyst support composition. Examples of such pore formers include, but are not limited to, cellulose, cellulose gel, microcrystalline cellulose, methyl cellulose, zinc stearate, flours, starches, modified starches, graphite, polymers, carbonates, bicarbonates, microcrystalline wax, or mixtures thereof. The amount of the pore former component used in this disclosure is in the range of from about 0.1 weight percent to about 30 weight percent (wt.%) based on the total weight of the components. Alternatively, the amount ranges from about 0.5 wt.% to about 30 wt.%, alternatively from about 0.1 wt.% to about 25 wt.%, alternatively from about 1 wt.% to about 25 wt.%, alternatively from about 1 wt.% to about 10 wt.%, alternatively from about 3 wt.% to about 6 wt.%, or alternatively from about 5 wt.% to about 20 wt.%. Variation in raw materials, such as particle size and particle morphology of the alumina or pore former can impact porosity and pore size distribution.

[0027] In an embodiment, the mixture can be formed into any suitable shape, which can be referred to herein generally as a shaped support. Examples of suitable shapes include round or spherical (e.g., spheres), ellipsoidal, pellets, cylinders, granules (e.g., regular and/or irregular), trilobe, quadrilobe, rings, wagonwheel and monoliths. In an embodiment, the mixture is formed into a LAPS. Herein a LAPS refers to a “rounded” particle shape characterized by an increased number of rounded surfaces in at least a portion of material. In an embodiment, the LAPS is a shape identified, based on computational processes, to be suitable for use in the disclosed methodologies. Such computational processes may be carried out using any suitable methodology (e.g., commercially available software package). Examples of LAPS include spheres and refined extrudates (e.g., ovoids, capsules, etc.). Methods for shaping particles include, for example, extrusion, spray drying, pelletizing, marumerizing, agglomeration, oil drop, and the like.

[0028] The roundness of the support may be further defined in this context in terms of contact angles along the exterior of the support. For example, it may be desired that no portion of the

exterior surface of the support (e.g., an apex of a protrusion) form an angle of less than 140 degrees with any other adjacent tangent of the exterior support. In this context, the portion and adjacent tangent forming the angle of measure are adjacent, meaning they have no space between them, such that the apex of the angle formed between the portions is located on the surface of the support. Other tolerances on the roundness of the support can also be specified, such as 130 degrees or 120 degrees in the above measure. Similarly, it may be desirable that the skin thickness of the catalyst be within a certain tolerance (e.g., less than about 400 microns). Subject to such constraints, the shape of the support under the present disclosure does not have to be spherical, it merely needs to have a nearly round surface with no corners as defined above. In other embodiments, a spherical or nearly spherical support is used.

[0029] In an embodiment, the mixture is formed into an extrudate via an extrusion processes employing an extruder, for example as described in U.S. Patent Nos. 5,558,851 and 5,514,362, each of which are incorporated herein in their entirety. In an embodiment, an extrudate can undergo further refining to form a LAPS such as a capsule, ellipsoid (e.g., ovoid or egg-shaped), etc. Examples of such refining techniques include milling, grinding, polishing, tumbling, compressing, briquetting, marumerizing, and spherodizing.

[0030] In an embodiment employing an extrusion process, the mixture further comprises an extrusion aid. An extrusion aid can function to improve the rheology of the mixture. This improvement in the rheology of the mixture can function to improve flow of the mixture through the extrusion die. Improved flow through the extrusion die can lead to easier equipment start-up, smoother extrusion, faster processing, lower extrusion pressures, and improved product appearance or physical properties. Extrusion aids, their effective amounts and methods of incorporation into the mixture can be varied and selected using any suitable methodology.

[0031] In an embodiment, the mixture is formed into a shaped support (e.g., having a LAPS such as a sphere) by an agglomeration process employing an agglomerator such as a pan or disc agglomerator, rotary drum agglomerator, briquetter, pin mixer, oil drop former etc. Any suitable agglomeration process can be employed for formation of shaped support (e.g., having a LAPS such as a sphere). For example, a spherical shaped support can be prepared by blending a pore former with the high surface area alumina (e.g., activated alumina and/or gamma alumina), under conditions sufficient to form a homogenous powder mixture. The homogenous powder mixture can then be introduced to an agglomerator such as a pan or disc agglomerator in the presence of

water. The amount of water should be sufficient to promote the formation of spheres having mechanical properties compatible with the disclosed processes and parameters. In an embodiment, the ratio of water: to homogenous powder mixture can be about 0.3-1.0:1, alternatively about 0.4-0.8:1 or alternatively about 0.6-0.7:1.

[0032] The spheres can have any residence time in the agglomerator suitable with some user and/or process goal. In an embodiment the user and/or process goal is to obtain a spheres having a diameter slightly larger than a desired final diameter of the support to take into account any shrinkage (e.g., from about 5% to about 15%, alternatively from about 5% to about 12%, alternatively from about 7% to about 12%, alternatively about 10%) that can occur in processing the shaped support (e.g., drying and/or calcining).

[0033] In an embodiment, the shaped support can be prepared from a high surface area alumina, for example a high surface area alumina comprising activated alumina, gamma alumina, rho alumina, boehmite, pseudoboehmite, bayerite or combinations thereof. In an embodiment, the shaped support can be prepared from an activated alumina. Herein an “activated alumina” refers to alumina prepared typically through the dehydration of aluminum hydroxide resulting in a high surface area, amorphous, rehydratable alumina material. In an alternative embodiment, the shaped support comprises gamma alumina, γ -alumina. Herein “ γ -alumina” refers to the alumina obtained typically via the thermal decomposition of pseudoboehmite or boehmite, resulting in an alumina material characterized by a metastable phase displaying low crystallinity and high surface area. High surface area herein refers to a surface area ranging from about 100 m²/g to about 400 m²/g, alternatively from about 150 m²/g to about 300 m²/g or alternatively from about 175 m²/g to about 275 m²/g.

[0034] In an embodiment, the shaped support comprises a high surface area alumina powder (e.g., activated alumina) having low levels of impurities such as sodium, silicon, iron and titanium. For example, the shaped support can comprise a high surface area alumina powder (e.g., activated alumina) having an impurity level of sodium, silicon, and iron less than about 10000 ppm, alternatively less than about 1000 ppm or alternatively less than about 10 ppm based on the total weight of the catalyst support. For example, the shaped support can comprise a high surface area alumina powder (e.g., activated alumina) having an impurity level of titanium less than about 4000 ppm, alternatively less than about 3000 ppm or alternatively less than about 2000 ppm based on the

total weight of the catalyst support. Such shaped supports can comprise alumina in any phase or mixture of phases compatible with the processes and parameters described herein.

[0035] Hereinafter, a mixture exiting a shaping process (e.g., extrusion, agglomeration, etc.) in the form of a shaped support (e.g., having a LAPS such as a sphere) shall be referred to as a “wet shaped support” or a “green shaped support.” As noted previously, such shaped supports can comprise high surface area alumina (e.g., activated alumina and/or gamma alumina), with the understanding that such alumina can be converted to other forms such as α -alumina via subsequent processing of the support as described herein (e.g., drying and/or calcining).

[0036] Excess water from the green shaped support can be removed by drying to form a dried support prior to further processing. Conventional methods for drying wet solids can be used to dry the green shaped support, and can include, for example drying in air or an inert gas such as nitrogen or helium. The air or inert gas can be circulating, moving, or static. Drying temperatures can range from about 200°F (93.3°C) to about 400°F (204.4°C), alternatively from about 200°F (93.3°C) to about 300°F (148.9°C), or alternatively from about 225°F (107.2°C) to about 275°F (135°C). Drying times can be equal to or greater than about 15 minutes, alternatively equal to or greater than about 1 hour, alternatively from about 1 hour to about 10 hours, alternatively from about 15 minutes to about 15 hours, alternatively from about 2 hours to about 5 hours, alternatively from about 1 hour to about 5 hours or alternatively from about 20 minutes to about 30 minutes.

[0037] In an embodiment, the dried support can be calcined to form a calcined support. Calcination temperatures can range from about 932°F (500°C) to about 2732°F (1500°C), alternatively from about 1292°F (700°C) to about 2552°F (1400°C), or alternatively from about 1562°F (850°C) to about 1372°F (1300°C).

[0038] Calcination times can range from about 0.5 hours to about 24 hours, alternatively from about 1 to about 18 hours, alternatively from about 0.5 hours to about 12 hours, alternatively from about 1 hour to about 6 hours, or alternatively from about 3 to 12 hours. In such embodiments, the calcination can be carried out in an oxygen containing atmosphere, for example dry air. As used herein “dry” air refers to air having a dew point of less than about 40°F. In an embodiment, the dried support can be calcined by exposing the materials to the temperature ranges disclosed herein in stages or steps. It is contemplated that any suitable calcination methodology compatible with the processes and materials disclosed herein can be employed.

[0039] In an embodiment, drying and/or calcining of a green shaped support results in a reduction in the particle size of the material. For example, drying and/or calcining of a spherical support can result in a dried and calcined support having a particle diameter ranging from about 1 mm to about 10 mm, alternatively from about 2 mm to about 7 mm, or alternatively from about 3 mm to about 5 mm.

[0040] In an embodiment, a calcined support of the type disclosed herein (e.g., having a LAPS such as a sphere) can be characterized by a crush strength ranging from about 1 lbf to about 50 lbf, alternatively from about 2 lbf to about 40 lbf, or alternatively from about 3 lbf to about 30 lbf. Herein the crush strength is defined as the resistance of the catalyst support and/or catalyst to compressive forces. Measurements of crush strength are intended to provide an indication of the ability of the catalyst to maintain its physical integrity during handling and use. Crush strength can be determined in accordance with ASTM method D 6175-98 "Standard Test Method for Radial Crush Strength of Extruded Catalyst" with the exception that the force applied to the sample is applied laterally using a flat platen.

[0041] The calcined support can be directly used in a catalyst preparation or can be further processed or otherwise used as described herein. A catalyst support prepared as described herein (e.g., shaped, dried, and calcined) is termed a prepared catalyst support, and such prepared catalyst supports can have any suitable composition (e.g., inorganic such as α -alumina) or shape (e.g., a LAPS such as a sphere) as described herein. Without intending to be limited by theory, a prepared catalyst support having a characteristic pore size distribution as described herein, can, in some embodiments and uses, display catalytic activity in the absence of any further processing (e.g., in the absence of the addition of one or more catalytic metals such as those described herein). Thus, without intending to be limited by theory, in some embodiments a prepared catalyst support having a characteristic pore size distribution as described herein, can be employed as a catalyst in a catalytic reaction of reactants under suitable reaction conditions.

[0042] In an embodiment, a method of preparing a selective hydrogenation catalyst comprises contacting a prepared catalyst support of the type disclosed herein (e.g., a shaped, dried, calcined support having a desired composition such as α -alumina, having a desired shape such as a sphere, and having a characteristic pore size distribution as described herein) with a chlorine-containing compound. The chlorine-containing compound can be a gas, a liquid, or combinations thereof. An embodiment comprises contacting the catalyst support with a liquid chlorine-containing compound

to create a chlorided catalyst support. Such a liquid can comprise at least one chlorine-containing compound. In some embodiments, the liquid chlorine-containing compound to which the prepared catalyst support can be exposed to create the chlorided catalyst support include, but are not limited to, hydrochloric acid; alkaline metal chloride; alkaline earth chloride; chlorohydrocarbons; compounds described by the formula $N(H_vR_wR'_xR''_yR'''_z)Cl$, where R, R', R'', and R''' is methyl, ethyl, propyl, butyl, or any combination thereof and v, w, x, y, z can be 0 to 4 provided $v+w+x+y+z = 4$; or combinations thereof. In some embodiments, the alkaline metal chloride can comprise potassium chloride, sodium chloride, lithium chloride, or combinations thereof. In some embodiments, the alkaline earth chloride can comprise calcium chloride, barium chloride, or combinations thereof. In some embodiments, compounds described by the formula $N(H_vR_wR'_xR''_yR'''_z)Cl$ can comprise ammonium chloride, methyl ammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, or combinations thereof. Chlorohydrocarbons as used herein can comprise compounds containing 1-10 carbons wherein there is at least one substitution of hydrogen for chlorine. In some embodiments chloro-hydrocarbons comprise compounds described by the formula CCl_xH_y (where $x + y = 4$); compounds described by the formula $C_2Cl_xH_y$ (where $x + y = 6$); or combinations thereof. In some embodiments compounds described by the formula CCl_xH_y comprise carbon tetrachloride, dichloromethane, or combinations thereof. In some embodiments, compounds described by the formula $C_2Cl_xH_y$ comprise trichloroethane. In an embodiment, the liquid chlorine-containing compound comprises potassium chloride in solution.

[0043] The prepared catalyst support can be contacted with the liquid chlorine-containing compound in any suitable manner. In an embodiment, the method used to contact a prepared catalyst support with a liquid chlorine-containing compound can be incipient wetness impregnation. During incipient wetness impregnation, the pores of the support become substantially filled with the liquid chlorine-containing compound. Other contacting methods such as soaking can also be employed to contact the prepared catalyst support with the liquid chlorine-containing compound to create a chlorided catalyst support.

[0044] An alternative embodiment comprises initially contacting the prepared catalyst support with a gaseous chlorine-containing compound to create a chlorided catalyst support. In some embodiments, the chlorine-containing compounds that can be employed as gases include, but are not limited to, hydrogen chloride gas, chlorine gas, CCl_xH_y (where $x + y = 4$), $C_2Cl_xH_y$ (where $x +$

y = 6), or combinations thereof. In another embodiment, the gaseous chlorine-containing compounds are obtained by heating a volatile chloro-hydrocarbon or mixture thereof.

[0045] A method used to contact a prepared catalyst support with a gaseous chlorine-containing compound can be accomplished by heating the prepared catalyst support in the presence of a gaseous chlorine-containing compound and optionally in the presence of oxygen, water, nitrogen, hydrogen or mixtures thereof to create a chlorided catalyst support. In an embodiment, the prepared catalyst support can be contacted with a gaseous chlorine-containing compound at temperatures of from about 572 °F (300°C) to about 1562 °F (850°C) for from about 0.2 hours to about 20 hours.

[0046] The amount of chlorine-containing compound deposited on the prepared catalyst support can be controlled independently of the contact method, whether by liquid contacting, gas phase contacting, or combinations thereof. The contacting method can deposit an amount of chlorine-containing compound such that the chlorided catalyst support, after exposure to a chlorine-containing compound, comprises from about 20 wt.% to about 0.001 wt.% chlorine based on a total weight of the chlorided catalyst support, alternatively from about 10 wt.% to about 0.01 wt.% chlorine, or alternatively from about 2 wt.% to about 0.05 wt.% chlorine.

[0047] After the prepared catalyst support has been contacted with the chlorine-containing compound to create the chlorided catalyst support, the chlorided catalyst support can be removed from contact with the chlorine-containing compound and processed to remove from the chlorided catalyst support unwanted elements such as an amount of chlorine-containing compound, decomposition products thereof, or other unwanted elements to create a clean chlorided catalyst support and otherwise prepare the chlorided catalyst support for further processing to produce a selective hydrogenation catalyst. Removing an amount of chlorine-containing compound and/or any other unwanted elements can occur via a wash, via vaporization, or combinations thereof, depending, for example, on the type of chlorine-containing compound involved. The vaporization can be accomplished at a temperature of from about 572 °F (300°C) to about 1562 °F (850°C) for from about 0.2 hours to about 20 hours. After processing, the clean chlorided catalyst support can comprise from about 0 to about 2000 ppm by weight of chlorine; alternatively, can comprise from about 1 ppm to about 1200 ppm by weight of chlorine; alternatively, from about 2 ppm to about 80 ppm by weight of chlorine; alternatively, from about 3 ppm to about 20 ppm, alternatively less than about 2 ppm by weight of chlorine with respect to the support.

[0048] In an embodiment, a chlorided catalyst support produced by contact with a liquid chlorine-containing compound can be exposed to an elevated temperature of from about 122°F (50°C) to about 1562°F (850°C) for from about 0.5 hours to about 20 hours to dry and/or calcine the chlorided catalyst support, thereby producing a cleaned chlorided catalyst support. In some embodiments, an optional washing step can follow the exposure to an elevated temperature. For example, the support can be washed with water at temperatures of from about 68°F (20°C) to about 212 °F (100°C) for from about 1 minute to about 2 hours. In an embodiment, the washing utilizes hot distilled or deionized water and occurs after drying and/or calcining. Following the washing step, the chlorided catalyst support can optionally undergo another exposure to an elevated temperature of from about 122°F (50°C) to about 1652°F (900°C) for from about 0.5 hours to about 20 hours to remove any unwanted moisture.

[0049] In another embodiment, a chlorided catalyst support produced by contact with a gaseous chlorine-containing compound can be cleaned via vaporization or washing or a combination thereof to remove an amount of chlorine-containing compound, decomposition products thereof, or other unwanted elements. In an embodiment, after contacting the catalyst support with the gaseous chlorine-containing compound, flow of the gaseous chlorine-containing compound is stopped, and the gaseous treated chlorided catalyst support can continue to be heated and/or calcined by exposure to an elevated temperature in the absence of the gaseous chlorine-containing compound to produce a cleaned chlorided catalyst support. Exposure to an elevated temperature can occur in the presence of oxygen, water, nitrogen and mixtures thereof for less than or equal to about 18 hours. This vaporization removal step can be optionally followed by exposing the chlorided catalyst support with a heated stream of gas free of the chlorine-containing compound to further remove any unwanted elements. After processing, the cleaned chlorided catalyst support can comprise from about 0 to about 2000 ppm by weight of chlorine; alternatively, can comprise from about 1ppm to about 1200 ppm by weight of chlorine; alternatively, from about 2 ppm to about 80 ppm by weight of chlorine; alternatively, from about 3 ppm to about 20 ppm, alternatively less than about 2 ppm by weight of chlorine with respect to the support.

[0050] In an embodiment, a method of preparing a hydrogenation catalyst comprises selecting an inorganic support having a multimodal distribution of pore diameters. In an embodiment, at least one distribution of pore diameters comprises pores having a diameter of equal to or greater than about 120 nm. In an alternative embodiment, at least one distribution of pore diameters

comprises pores having a diameter of equal to or greater than about 200 nm. The selected support can then be treated as a catalyst support of the type disclosed herein and subjected to the processing disclosed herein (e.g., drying, calcining, chloriding).

[0051] In an embodiment, a method of preparing a selective hydrogenation catalyst comprises contacting a cleaned chlorided catalyst support of the type disclosed herein with at least one catalytically active metal, alternatively palladium. The palladium can be added to the cleaned chlorided catalyst support by contacting the cleaned chlorided catalyst support with a palladium-containing compound to form a palladium supported composition as will be described in more detail later herein. Examples of suitable palladium-containing compounds include without limitation palladium chloride, palladium nitrate, ammonium hexachloropalladate, ammonium tetrachloropalladate, palladium acetate, palladium bromide, palladium iodide, tetraamminepalladium nitrate, or combinations thereof. In an embodiment, the palladium-containing compound is a component of an aqueous solution. An example of palladium-containing solution suitable for use in this disclosure includes without limitation a solution comprising palladium metal.

[0052] In an embodiment, palladium is present in the mixture for preparation of a selective hydrogenation catalyst in an amount of from about 0.005 wt.% to about 2 wt.%, alternatively from about 0.005 wt.% to about 1 wt.% or alternatively from about 0.005 wt.% to about 0.5wt.% based on the total catalyst weight.

[0053] In an embodiment, a method of preparing a selective hydrogenation catalyst can initiate with the contacting of cleaned chlorided catalyst support with a palladium-containing compound to form a supported palladium composition. The contacting can be carried out using any suitable technique. For example, the cleaned chlorided catalyst support can be contacted with the palladium-containing compound by soaking, or incipient wetness impregnation of the support with a palladium-containing solution. In such embodiments, the resulting supported palladium composition can have greater than about 90 wt.%, alternatively from about 92 wt.% to about 98 wt.%, alternatively from about 94 wt.% to about 96 wt.% of the palladium concentrated near the periphery of the palladium supported composition, as to form a palladium skin. In an embodiment, the cleaned chloride catalyst support is contacted with the palladium-containing solution by soaking the support in the palladium-containing solution.

[0054] The palladium skin can be any thickness as long as such thickness can promote the hydrogenation processes disclosed herein. Generally, the thickness of the palladium skin can be in

the range of from about 1 micron to about 3000 microns, alternatively from about 5 microns to about 2000 microns, alternatively from about 10 microns to about 1000 microns, alternatively from about 50 microns to about 500 microns. Examples of such methods are further described in more details in U.S. Patent Nos. 4,404,124 and 4,484,015, each of which is incorporated by reference herein in its entirety.

[0055] Any suitable method can be used for determining the concentration of the palladium in the skin of the palladium supported composition and/or the thickness of the skin. For example, one method involves breaking open a representative sample of the palladium supported composition particles and treating the palladium supported composition particles with a dilute alcoholic solution of N,N-dimethyl-para-nitrosoaniline. The treating solution reacts with the palladium to give a red color that can be used to evaluate the distribution of the palladium. Yet another technique for measuring the concentration of the palladium in the skin of the palladium supported composition involves breaking open a representative sample of catalyst particles, followed by treating the particles with a reducing agent such as hydrogen to change the color of the skin and thereby evaluate the distribution of the palladium. Alternatively, the palladium skin thickness can be determined using electron probe microanalysis.

[0056] The supported palladium composition formed by contacting the cleaned chlorided catalyst support with the palladium-containing solution optionally can be dried at a temperature of from about 59°F (15°C) to about 302°F (150°C), alternatively from about 86°F (30°C) to about 212 °F (100°C), alternatively from about 140°F (60°C) to about 212°F (100°C); and for a period of from about 0.1 hour to about 100 hours, alternatively from about 0.5 hour to about 20 hours, alternatively from about 1 hour to about 10 hours. Alternatively, the palladium supported composition can be calcined. This calcining step can be carried out at temperatures up to about 1562 °F (850°C), alternatively of from about 302°F (150°C) to about 1472 °F (800°C), alternatively from about 302 °F (150°C) to about 1382 °F (750°C), alternatively from about 302°F (150°C) to about 1292°F (700°C); and for a period of from about 0.2 hour to about 20 hours, alternatively from about 0.5 hour to about 20 hours, alternatively from about 1 hour to about 10 hours.

[0057] In an embodiment, the selective hydrogenation catalyst can further comprise one or more selectivity enhancers. Suitable selectivity enhancers include, but are not limited to, Group 1B metals, Group 1B metal compounds, silver compounds, fluorine, fluoride compounds, sulfur, sulfur compounds, alkali metals, alkali metal compounds, alkaline metals, alkaline metal

compounds, iodine, iodide compounds, or combinations thereof. In an embodiment, the selective hydrogenation catalyst comprises one or more selectivity enhancers which can be present in total in the mixture for preparation of the selective hydrogenation catalyst in an amount of from about 0.001 wt.% to about 10 wt.% based on the total weight of the selective hydrogenation catalyst, alternatively from about 0.01 wt.% to about 5 wt.%, alternatively from about 0.01 wt.% to about 2 wt.%. The amount of selectivity enhancer incorporated into the selective hydrogenation catalyst can be in the range described herein for the amount of selectivity enhancer used to prepare the selective hydrogenation catalyst.

[0058] In an embodiment, the selectivity enhancer comprises silver (Ag), silver compounds, or combinations thereof. Examples of suitable silver compounds include without limitation silver nitrate, silver acetate, silver bromide, silver chloride, silver iodide, silver fluoride, or combinations thereof. In an embodiment, the selectivity enhancer comprises silver nitrate. The selective hydrogenation catalyst can be prepared using silver nitrate in an amount of from about 0.005 wt.% to about 5 wt.% silver based on the total weight of the selective hydrogenation catalyst, alternatively from about 0.01 wt.% to about 1 wt.% silver, alternatively from about 0.05 wt.% to about 0.5 wt.%. The amount of silver incorporated into the selective hydrogenation catalyst can be in the range described herein for the amount of silver nitrate used to prepare the selective hydrogenation catalyst.

[0059] In an embodiment, the selectivity enhancer comprises alkali metals, alkali metal compounds, or combinations thereof. Examples of suitable alkali metal compounds include without limitation elemental alkali metal, alkali metal halides (e.g., alkali metal fluoride, alkali metal chloride, alkali metal bromide, alkali metal iodide), alkali metal oxides, alkali metal carbonate, alkali metal sulfate, alkali metal phosphate, alkali metal borate, or combinations thereof. In an embodiment, the selectivity enhancer comprises potassium fluoride (KF). In another embodiment, the selective hydrogenation catalyst is prepared using an alkali metal compound in an amount of from about 0.01 wt.% to about 5 wt.% based on the total weight of the selective hydrogenation catalyst, alternatively from about 0.03 wt.% to about 2 wt.%, alternatively from about 0.05 wt.% to about 1 wt.%. The amount of alkali metal incorporated into the selective hydrogenation catalyst can be in the range described herein for the amount of alkali metal compound used to prepare the selective hydrogenation catalyst.

[0060] In some embodiments, one or more selectivity enhancers of the type described previously herein can be added to the supported palladium composition. In an embodiment, silver can be added to the supported palladium composition. For example, the supported palladium composition can be placed in an aqueous silver nitrate solution of a quantity greater than that necessary to fill the pore volume of the composition. The resulting material is a palladium/silver supported composition (herein this particular embodiment of the selective hydrogenation catalyst is referred to as a Pd/Ag composition). The Pd/Ag composition can be dried and/or calcined as previously described herein.

[0061] In an embodiment, one or more alkali metals can be added to the Pd/Ag composition using any suitable technique such as those described previously herein. In an embodiment, the selectivity enhancer comprises potassium fluoride, and the resulting material is a palladium/silver/alkali metal fluoride supported composition (herein this particular embodiment of the selective hydrogenation catalyst is referred to as a Pd/Ag/KF composition).

[0062] In an embodiment, the supported palladium composition is contacted with both an alkali metal halide and a silver compound. Contacting the supported palladium composition with both an alkali metal halide and a silver compound can be carried out simultaneously; alternatively the contacting can be carried out sequentially in any user-desired order.

[0063] In an embodiment, a selective hydrogenation catalyst formed in accordance with the methods disclosed herein comprises an α -alumina support of the type disclosed herein, palladium, and one or more selectivity enhancers, (e.g., silver and/or potassium fluoride). The selective hydrogenation catalyst (Pd/Ag, Pd/KF, and/or the Pd/Ag/KF/ compositions) can be dried to form a dried selective hydrogenation catalyst. In some embodiments, this drying step can be carried out at a temperature in the range of from about 32°F (0°C) to about 302°F (150°C), alternatively from about 86°F (30°C) to about 212°F (100°C), alternatively from about 122°F (50°C) to about 176°F (80°C); and for a period of from about 0.1 hour to about 100 hours, alternatively from about 0.5 hour to about 20 hours, alternatively from about 1 hour to about 10 hours.

[0064] The dried selective hydrogenation catalyst can be reduced using hydrogen gas or a hydrogen gas containing feed, e.g., the feed stream of the selective hydrogenation process, thereby providing for optimum operation of the selective hydrogenation process. Such a gaseous hydrogen reduction can be carried out at a temperature in the range of from, for example, about 32°F (0°C) to

about 752°F (400°C), alternatively 68°F (20°C) to about 572°F (300°C), or alternatively about 86°F (30°C) to about 482°F (250°C).

[0065] In an embodiment, a selective hydrogenation catalyst of the type disclosed herein can catalyze a selective hydrogenation process. In some embodiments a selective hydrogenation catalyst of the type disclosed herein is used in conjunction with one or more conventional hydrogenation catalysts to catalyze a selective hydrogenation process. In such embodiments having a conventional hydrogenation catalyst and a selective hydrogenation catalyst of the type disclosed herein, the selective hydrogenation catalyst can be present in an amount that comprises greater than about 50% of the total amount of hydrogenation catalyst present during the selective hydrogenation process. Alternatively greater than about 70% or alternatively greater than about 85%. Herein, the phrase “conventional hydrogenation catalysts” refers to hydrogenation catalysts that lack a catalyst support of the type disclosed herein.

[0066] The selective hydrogenation catalyst can be contacted with an unsaturated hydrocarbon stream primarily containing unsaturated hydrocarbons, e.g., ethylene, but also containing a highly unsaturated hydrocarbon, e.g., acetylene. The contacting can be executed in the presence of hydrogen at conditions effective to selectively hydrogenate the highly unsaturated hydrocarbon to an unsaturated hydrocarbon. In an embodiment, the selective hydrogenation catalysts of the type disclosed herein are used in the hydrogenation of highly unsaturated hydrocarbons such as for example and without limitation acetylene, methylacetylene, propadiene, butadiene or combinations thereof. As used herein, a highly unsaturated hydrocarbon is defined as a hydrocarbon containing a triple bond, two conjugated carbon-carbon double bonds, or two cumulative carbon-carbon double bonds. As used herein, an unsaturated hydrocarbon is defined as a hydrocarbon containing an isolated carbon-carbon double bond. Figure 1 illustrates an embodiment of a hydrogenation process that utilizes a selective hydrogenation catalyst of the type disclosed herein. The hydrogenation process includes feeding an unsaturated hydrocarbon stream 10 and a hydrogen (H₂) stream 20 to a hydrogenation reactor 30 within which the selective hydrogenation catalyst is disposed. The unsaturated hydrocarbon stream 10 primarily comprises one or more unsaturated hydrocarbons, but it can also contain one or more highly unsaturated hydrocarbons such as for example and without limitation acetylene, methylacetylene, propadiene, and butadiene. Alternatively, unsaturated hydrocarbon stream 10 and hydrogen stream 20 can be combined in a single stream that is fed to hydrogenation reactor 30.

[0067] In an embodiment, reactor 30 is a selective hydrogenation reactor that can belong to an acetylene removal unit of an unsaturated hydrocarbon production plant in a backend configuration. As used herein, “backend” refers to the location of the acetylene removal unit in an unsaturated hydrocarbon production unit that receives the lower boiling fraction from a deethanizer fractionation tower that receives the higher boiling fraction from a demethanizer fractionation tower which receives a feed from an unsaturated hydrocarbon production process.

[0068] In an embodiment, reactor 30 is a selective hydrogenation reactor that can belong to an acetylene removal unit of an unsaturated hydrocarbon production plant in a frontend deethanizer configuration. As used herein, “frontend deethanizer” refers to the location of the acetylene removal unit in an unsaturated hydrocarbon production unit that receives the lower boiling fraction from a deethanizer fractionation tower that receives a feed from an unsaturated hydrocarbon production process.

[0069] In an embodiment, reactor 30 is a selective hydrogenation reactor that can belong to an acetylene removal unit of an unsaturated hydrocarbon production plant in a frontend depropanizer configuration. As used herein, “frontend depropanizer” refers to the location of the acetylene removal unit in an unsaturated hydrocarbon production unit that receives the lower boiling fraction from a depropanizer fractionation tower that receives a feed from an unsaturated hydrocarbon production process.

[0070] In an embodiment, reactor 30 is a selective hydrogenation reactor that can belong to an acetylene removal unit of an unsaturated hydrocarbon production plant in a raw gas configuration. As used herein, “raw gas” refers to the location of the acetylene removal unit in an unsaturated hydrocarbon production unit that receives a feed from an unsaturated hydrocarbon production process without any intervening hydrocarbon fractionation.

[0071] It is understood that hydrogenation reactor 30, and likewise the selective hydrogenation catalysts disclosed herein, are not limited to use in backend acetylene removal units, frontend deethanizer units, frontend depropanizer, or raw gas units and can be used in any process wherein a highly unsaturated hydrocarbons contained within an unsaturated hydrocarbon stream is selectively hydrogenated to a unsaturated hydrocarbon. In frontend deethanizer units, frontend depropanizer, or raw gas units, the unsaturated hydrocarbon stream 10 contains sufficient quantities of hydrogen for the hydrogenation reaction, and a hydrogen stream 20 can become unnecessary for the reaction.

[0072] In those embodiments wherein the acetylene removal unit is in a backend configuration, the highly unsaturated hydrocarbon being fed to the hydrogenation reactor 30 comprises acetylene. The mole ratio of the hydrogen to the acetylene being fed to hydrogenation reactor 30 can be in the range of from about 0.1 to about 10, alternatively from about 0.2 to about 5, alternatively from about 0.5 to about 4.

[0073] In those embodiments wherein the acetylene removal unit is in a front end deethanizer, front-end depropanizer or raw gas configuration, the highly unsaturated hydrocarbon being fed to the hydrogenation reactor 30 comprises acetylene. In such an embodiment, the mole ratio of the hydrogen to the acetylene being fed to the hydrogenation reactor 30 can be in the range of from about 10 to about 3000, alternatively from about 10 to about 2000, alternatively from about 10 to about 1500.

[0074] In those embodiments wherein the acetylene removal unit is in a front-end depropanizer or raw gas configuration, the highly unsaturated hydrocarbon being fed to the hydrogenation reactor 30 comprises methylacetylene. In such an embodiment, the mole ratio of the hydrogen to the methylacetylene being fed to the hydrogenation reactor 30 can be in the range of from about 3 to about 3000, alternatively from about 5 to about 2000, alternatively from about 10 to about 1500.

[0075] In those embodiments wherein the acetylene removal unit is in a front-end depropanizer or raw gas configuration, the highly unsaturated hydrocarbon being fed to the hydrogenation reactor 30 comprises propadiene. In such an embodiment, the mole ratio of the hydrogen to the propadiene being fed to the hydrogenation reactor 30 can be in the range of from about 3 to about 3000, alternatively from about 5 to about 2000, alternatively from about 10 to about 1500.

[0076] In another embodiment, reactor 30 can represent a plurality of reactors. The plurality of reactors can optionally be separated by a means to remove heat produced by the reaction. The plurality of reactors can optionally be separated by a means to control inlet and effluent flows from reactors or heat removal means allowing for individual or alternatively groups of reactors within the plurality of reactors to be regenerated. The selective hydrogenation catalyst can be arranged in any suitable configuration within hydrogenation reactor 30, such as a fixed catalyst bed. Carbon monoxide can also be fed to reactor 30 via a separate stream (not shown), or it can be combined with hydrogen stream 20. In an embodiment, the amount of carbon monoxide being fed to reactor 30 during the hydrogenation process is less than about 0.15 mole percent (mol.%) based on the total moles of fluid being fed to reactor 30.

[0077] Hydrogenation reactor 30 can be operated at conditions effective to selectively hydrogenate highly unsaturated hydrocarbons to one or more unsaturated hydrocarbons upon contacting the selective hydrogenation catalyst in the presence of the hydrogen. The conditions are desirably effective to maximize hydrogenation of highly unsaturated hydrocarbons to unsaturated hydrocarbons and to minimize hydrogenation of highly unsaturated hydrocarbons to saturated hydrocarbons. In some embodiments, acetylene can be selectively hydrogenated to ethylene. Alternatively methylacetylene can be selectively hydrogenated to propylene; alternatively propadiene can be selectively hydrogenated to propylene. Alternatively, butadiene can be selectively hydrogenated to butenes. In some embodiments, the temperature within the hydrogenation zone can be in the range of from about 41°F (5°C) to about 572°F (300°C), alternatively from about 50°F (10°C) to about 482°F (250°C), alternatively from about 59°F (15°C) to about 392°F (200°C). In some embodiments, the pressure within the hydrogenation zone can be in the range of from about 15 (204 kPa) to about 2,000 (13,890 kPa) pounds per square inch gauge (psig), alternatively from about 50 psig (446 kPa) to about 1,500 psig (10,443 kPa), alternatively from about 100 psig (790 kPa) to about 1,000 psig (6,996 kPa).

[0078] Referring back to Figure 1, an effluent stream 40 comprising unsaturated hydrocarbons, including the one or more monoolefins produced in hydrogenation reactor 30, and any unconverted reactants exit hydrogenation reactor 30. In an embodiment where hydrogenation reactor 30 is in a backend acetylene removal unit configuration, effluent stream 40 primarily comprises ethylene comprises less than about 5 ppm, alternatively less than about 1 ppm of highly unsaturated hydrocarbons. In embodiments wherein hydrogenation reactor 30 is in a frontend deethanizer, frontend depropanizer, or raw gas acetylene removal unit configuration, effluent stream 40 primarily comprises ethylene comprises less than about 5 ppm, alternatively less than about 1 ppm of acetylene, while other highly unsaturated hydrocarbons such as methylacetylene or propadiene comprises less than about 5000 ppm, alternatively less than about 4000 ppm.

[0079] In an embodiment, a selective hydrogenation catalyst of the type described herein can have a comparable catalytic activity when compared to an otherwise similar catalyst lacking a catalyst support of the type described herein. For example, a selective hydrogenation catalyst of this disclosure can have at least one performance property that is improved when compared to an otherwise similar catalyst. In an embodiment, a selective hydrogenation catalyst of this disclosure has an optimal balance of desirable properties. For example, a selective hydrogenation catalyst of

the type disclosed herein has a catalytic activity or clean up temperature comparable to an otherwise similar catalyst. The comparable catalytic activity can translate to a comparable clean up temperature. Hereinafter, an otherwise similar catalyst refers to a selective hydrogenation catalyst comprising an inorganic catalyst support, palladium and one or more selectivity enhancers but lack a catalyst support of the type disclosed herein. Herein, the cleanup temperature is referred to as T1 and refers to the temperature at which the acetylene concentration drops below 20 ppm in the effluent when processing a representative frontend deethanizer, frontend depropanizer, or raw gas acetylene removal unit feed stream comprising unsaturated hydrocarbon and highly unsaturated hydrocarbons such as acetylenes and diolefins. Determinations of T1 are described in more detail for example in U.S. Patent Nos. 7,417,007 and 6,417,136, each of which are incorporated herein in their entirety. In an embodiment, a selective hydrogenation catalyst of the type disclosed herein can have a T1 of from about 80°F (26.7°C) to about 160°F (71.1°C), alternatively from about 85°F (29.4°C) to about 150°F (65.6°C), alternatively from about 90°F (32.2°C) to about 140°F (60°C) for fresh catalyst. In an embodiment, a selective hydrogenation catalyst of the type described herein can display a selectivity window that is increased when compared to an otherwise similar catalyst lacking a catalyst support of the type described herein. Herein, a selectivity window refers to the reaction time period over which the catalyst displays a desired selectivity for a specified reaction. For example, a selective hydrogenation catalyst of the type disclosed herein when employed as a catalyst in acetylene hydrogenation reactors can display a selectivity window for ethylene of equal to or greater than about 200 hours, alternatively equal to or greater than about 250 hours, or alternatively equal to or greater than about 300 hours. The selectivity window of selective hydrogenation catalysts of the type disclosed herein can be increased by equal to or greater than about 50%, alternatively equal to or greater than about 75%, or alternatively equal to or greater than about 100% when compared to an otherwise similar catalyst lacking a catalyst support of the type disclosed herein. Alternatively, the selectivity window of selective hydrogenation catalysts of the type disclosed herein can be increased by equal to or greater than about 50%, alternatively equal to or greater than about 75%, or alternatively equal to or greater than about 100% when compared to an otherwise identical catalyst lacking a catalyst support of the type disclosed herein.

[0080] In an embodiment, a selective hydrogenation catalyst of the type disclosed herein can have an operating window of from about 35°F (1.7°C) to about 120°F (48.9°C), alternatively from

about 40 °F (4.4°C) to about 80°F (26.7 °C), or alternatively from about 45 °F (7.2°C) to about 60°F (15.6 °C). The operating window of a selective hydrogenation catalyst of the type described herein can be increased by greater than about 10%, alternatively greater than about 15%, alternatively greater than about 20% when compared to an otherwise similar catalyst prepared in the absence of catalyst support of the type described herein. Alternatively, the operating window of a selective hydrogenation catalyst of the type described herein can be increased by greater than about 10%, alternatively greater than about 15%, alternatively greater than about 20% when compared to an otherwise identical catalyst prepared in the absence of catalyst support of the type described herein. An operating window (ΔT) is defined as the difference between a runaway temperature (T_2) at which 3 wt.% of ethylene is hydrogenated from a feedstock comprising highly unsaturated and unsaturated hydrocarbons, and the cleanup temperature (T_1). ΔT is a convenient measure of the catalysts selectivity window and operation stability in the hydrogenation of highly unsaturated hydrocarbons (e.g., acetylene) to unsaturated hydrocarbons (e.g., ethylene). The more selective a catalyst, the higher the temperature beyond T_1 required to hydrogenate a given unsaturated hydrocarbons (e.g., ethylene). The T_2 is coincident with the temperature at which a high probability of runaway ethylene hydrogenation reaction could exist in an adiabatic reactor. Therefore, a larger ΔT translates to a more selective catalyst and a wider operation window for the complete acetylene hydrogenation.

[0081] In an embodiment, a selective hydrogenation catalyst is formed from a prepared catalyst support having a LAPS. Such catalysts, designated LAPS selective hydrogenation catalysts, can display improved physical and mechanical properties when compared to catalysts formed from supports having shapes other than a LAPS.

[0082] In an embodiment a LAPS selective hydrogenation catalyst is characterized by an increased structural integrity when compared to a selective hydrogenation catalyst formed from supports having shapes other than a LAPS. The increased structural integrity of the LAPS selective hydrogenation catalyst can be reflected in the decreased attrition of the material in comparison to a selective hydrogenation catalyst formed from supports having shapes other than a LAPS. Herein attrition refers to the propensity of a material to produce fines in the course of transportation, handling, and use and can be determined in accordance with ASTM D 4058. For example the LAPS selective hydrogenation catalysts can have an attrition rate ranging from about

0.05% to about 5%, alternatively from about 0.1% to about 3%, or alternatively from about 0.15% to about 2%.

[0083] In an embodiment, selective hydrogenation catalysts formed from a catalyst support of the type disclosed herein (e.g., having a multimodal distribution of pore diameters) can advantageously exhibit a decreased fouling rate when operated under the same selective hydrogenation conditions, and when compared to an otherwise similar catalyst prepared in the absence of a catalyst support having a multimodal distribution of pore diameters. The reduced fouling rate can result in a catalyst lifetime that is increased by from about 5% to about 500%, alternatively from about 10 % to about 120%, or alternatively from about 20% to about 40% when compared to a selective hydrogenation catalyst formed in the absence of a catalyst support of the type disclosed herein. For example, a selective hydrogenation catalyst of this disclosure can exhibit an improved catalyst lifetime when operated under the same selective hydrogenation conditions, and when compared to an otherwise similar catalyst prepared in the absence of a catalyst support having a multimodal distribution of pore diameters. Herein the lifetime refers to the period of time over which the catalyst can function as a selective hydrogenation catalyst that can be regenerated when spent to some user and/or process desired catalytic activity.

[0084] In an embodiment, selective hydrogenation catalysts formed from a catalyst support of the type disclosed herein (e.g., having a multimodal distribution of pore diameters) can advantageously exhibit an extended length of time between regeneration cycles when operated under the same selective hydrogenation conditions and regenerated under the same regeneration conditions, when compared to an otherwise similar catalyst prepared in the absence of a catalyst support having a multimodal distribution of pore diameters. Regeneration of the selective hydrogenation catalyst is carried out when the catalyst activity reaches a point at which it no longer efficiently catalyzes a particular process (e.g., selective hydrogenation), the catalyst can be at the end of its life or at the end of one of its cycles of catalyst activity. If the catalyst has one or more cycles of catalyst activity remaining, the catalyst can be regenerated to begin a new cycle of catalyst activity. Increasing the length of the catalyst cycle, i.e., the time period between regeneration of the catalysts, and/or increasing the number of cycles can significantly improve the overall economics of the catalyzed process. In an embodiment, a selective hydrogenation catalyst of the type disclosed herein can have an increased length of time between regeneration cycles

ranging from about 5% to about 500%, alternatively from about 10% to about 100%, or alternatively from about 40% to about 70%.

[0085] In an embodiment, a selective hydrogenation catalyst of the type disclosed herein provides for improved control of pressure drop build-up. Pressure drop build-up in the catalyst bed is attributable to a variety of factors including the deposition of feed contaminants, crust formation, catalyst milling and the presence of corrosion products. Pressure drop build-up can lead to adverse events during the hydrogenation process including but not limited to channeling or bypassing, high-radial temperature spread, operating difficulties and maldistribution.

EXAMPLES

[0086] The disclosure having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification of the claims to follow in any manner.

Example 1

[0087] This example illustrates the preparation of various palladium-containing catalyst compositions to be used in a hydrogenation process. Catalysts A thru E were prepared as follows: an α -alumina support having a surface area ranging from 5 m²/g to 12 m²/g was supplied by BASF and was chloride-treated, followed by the addition of palladium and silver as described herein.

[0088] Tables 1, 2, and 3 summarize the physical properties of catalysts A thru E. Figures 2-6 show the pore size distribution from mercury porosimetry for catalysts A thru E. The dashed lines represent the sample distributions while the solid line represents percentage cumulative intrusion.

Table 1

Catalyst	Form	Pd (ppm)	Ag (ppm)	Surface Area (m ² /g) ¹
A	extrudate	252	1718	9.57
B	extrudate	284	2492	8.12
C	extrudate	308	1869	8.57
D	pellet	267	1840	6.71
E	extrudate	307	1889	11.22

Pellets were ~4mm x 4mm extrudates were ~5mm x 3mm

¹ By Brunauer, Emmett, and Teller method

Table 2

Catalyst	RANGE 1		RANGE 2		RANGE 3		RANGE 4	
	Pore size Diameter range (nm)	% total pore volume	Pore size Diameter range (nm)	% total pore volume	Pore size Diameter range (nm)	% total pore volume	Pore size Diameter range (nm)	% total pore volume
A	29736 to 2000	0.51	--	--	2000 to 45	94.29	45 to 10	5.2
B	21409 to 2,000	0.15	2000 to 332	19.32	332 to 35	80.53	--	--
C	21449 to 230	24.7	--	--	230 to 30	74.56	30 to 10	0.74
D	21464 to 280	23.9	--	--	280 to 30	76.1	--	--
E	21469 to 280	17.53	--	--	280 to 36	76.87	36 to 10	5.6

Table 3

Catalyst	Form	Surface Area (m ² /g) ¹	Pore volume (cc/g) ²
A	extrudate	9.57	0.326
B	extrudate	8.12	0.344
C	extrudate	8.57	0.253
D	pellet	6.71	0.212
E	extrudate	11.22	0.265

¹ By Brunauer, Emmett, and Teller method² By ASTM UOP578-02

Example 2

[0089] Catalyst performance runs were made as follows: About 20 mL of catalyst was mixed with 40 mL of alundum and placed in a stainless steel jacketed reactor tube having a 0.692 inch inner diameter and a length of about 18 inches. The catalyst resided in the middle of the reactor and both ends of the reactor were packed with about 10 mL of alundum. The reaction temperature was controlled by circulating ethylene glycol through the jacket of the reactor tube. The catalyst was then activated with hydrogen at a flow rate of 200 mL/min at atmospheric pressure at the listed temperature for two hours. The catalyst was then contacted with the feed gas (approximately: 13 wt.% methane, 85.8 wt.% ethylene, 1.2 wt.% acetylene, and 0.1 wt.% hydrogen) at about 913 mL/min at 200 psig. Some runs used a higher hydrogen concentration and are noted likewise. The reaction temperature was adjusted to yield an acetylene conversion of about 90%. Conversion is referred to as the disappearance of acetylene. Gas analysis was performed by gas chromatography using a KCl-Al₂O₃ PLOT column. Figure 7 shows the temperature needed to maintain a 90% conversion of acetylene as a function of time. Figure 8 shows the selectivity to ethylene as a function of time.

[0090] The selectivity (sel.) to ethylene was also calculated using the following set of equations, where “C₄” represents butane, butenes and butadiene and where “heavies” refer to hydrocarbons having more carbon atoms than C₄:

$$\text{selectivity to ethane} = (\text{weight of ethane made} / \text{weight of acetylene consumed}) * 100$$

$$\text{selectivity to C}_4\text{'s} = (\text{weight of C}_4\text{'s made} / \text{weight of acetylene consumed}) * 100$$

$$\text{selectivity to heavies} = (\text{weight of heavies made} / \text{weight of acetylene consumed}) * 100$$

$$\text{selectivity to ethylene} = 100 - \text{sel. to ethane} - \text{sel. to C}_4\text{'s} - \text{sel. to heavies}$$

[0091] The results demonstrate that while all the catalysts displayed good activity as indicated by the comparable temperatures at time zero, catalysts of the type disclosed herein (i.e., catalysts C, D, and E) displayed a leveling of the adjusted temperature, Figure 7. This in contrast to catalysts A and B which do not have a catalyst support with a pore distribution of the type disclosed herein. In the case of catalysts A and B, the temperature begins to increase toward the end of the run. Further, referring to Figure 8, with regards to selectivity catalysts C, D, and E displayed an increased selectivity as indicated by a plateau in selectivity over the time period investigated. In contrast, catalysts A and B show a decline in selectivity after about 150 hours. Catalysts C, D, and E are selective hydrogenation catalysts having a pore size distribution, specifically the presence of the peak around 1,000 nm in the pore size distribution while catalysts A and B do not have this peak.

Example 3

[0092] A catalyst support comprising a spherical LAPS was prepared as follows: CP-5 was used as the starting material. CP-5 alumina is an activated alumina powder commercially available from BASF and has a surface area of 270 m²/g, a packed bulk density of 38 lb/ft³, and a particle size distribution where the average size is 5 microns and 90 wt.% of the materials is less than 12 microns. The total water content of the alumina was determined to be 10%. A mixture of 400 grams of activated alumina and 70 grams of pore-former was blended for approximately 60 minutes to achieve a homogeneous powder mix. The total water content of the blended powder was determined to be 10 wt.% by loss on ignition (e.g., 1 hour at 1000°C). The combined mixture was fed to a pan agglomerator while spraying in a continuous water stream over a period of about 6 hours. The water/powder ratio of the feeds was held constant over this time at approximately 0.65:1. The spheres were removed after they had grown to a size of approximately 4 mm diameter using the described agglomeration technique. The resulting

spheres were dried at 110°C for 15 hours. The dried spheres were calcined in air for 3 hours at 1160°C to produce a spherical LAPS catalyst support having a BET surface area of 11 m²/gram, a crush strength of 12 lbf, a particle diameter range of 3-5 mm and a Hg pore volume of 0.65 cc/gram. A plot of the incremental Intrusion Volume as a function of pore size is presented in Figure 9.

Example 4

[0093] A selective hydrogenation catalyst is prepared using the alumina spheres of Example 3 as follows: the alumina spheres of Example 3 are chloride-treated, followed by the addition of palladium and silver as described herein to form a selective hydrogenation catalyst. Catalyst performance runs are made as follows: catalyst is mixed with alundum and placed in a jacketed reactor tube. The catalyst is then activated with hydrogen. The catalyst is then contacted with the feed gas (comprising methane, ethylene, acetylene, and hydrogen). The reaction temperature is adjusted to yield an acetylene conversion of about 90%. Conversion is referred to as the disappearance of acetylene. Additional investigations of catalyst behavior (e.g., activity, regeneration cycle length, expected catalyst lifetime) are performed.

ADDITIONAL EMBODIMENTS

[0094] The following enumerated embodiments are provided as non-limiting examples:

[0095] A first embodiment which is a composition comprising a support formed from a high surface area alumina and having a low angularity particle shape; and at least one catalytically active metal, wherein the support has pores, a total pore volume, and a pore size distribution; wherein the pore size distribution displays at least two peaks of pore diameters, each peak having a maximum; wherein a first peak has a first maximum of pore diameters of equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters of less than about 200 nm; and wherein greater than or equal to about 5% of a total pore volume of the support is contained within the first peak of pore diameters.

[0096] A second embodiment which is the composition of the first embodiment wherein the low angularity particle shape is a sphere.

[0097] A third embodiment which is the composition of the first embodiment wherein the low angularity particle shape is a refined extrudate.

[0098] A fourth embodiment which is the composition of any preceding embodiment wherein the high surface area alumina comprises activated alumina, gamma alumina, rho alumina, boehmite, psuedoboehmite, bayerite, or combinations thereof.

[0099] A fifth embodiment which is the composition of any of the first through third embodiments wherein the high surface area alumina consists essentially of activated alumina and/or gamma alumina.

[00100] A sixth embodiment which is the composition of any preceding embodiment wherein the first maximum of the first peak of pore diameters is from about 200 nm to about 9000 nm.

[00101] A seventh embodiment which is the composition of any preceding embodiment wherein greater than or equal to about 10% of the total pore volume of the support is contained within the first peak of pore diameters.

[00102] An eighth embodiment which is the composition of any preceding embodiment wherein the first maximum of the first peak of pore diameters is from about 400 nm to about 8000 nm.

[00103] A ninth embodiment which is the composition of any preceding embodiment wherein greater than or equal to about 15% of the total pore volume of the support is contained within the first peak of pore diameters.

[00104] A tenth embodiment which is the composition of any preceding embodiment having a surface area of from about 1 m²/g to about 35 m²/g.

[00105] An eleventh embodiment which is the composition of any preceding embodiment having a total pore volume of from about 0.1 cc/g to about 0.9 cc/g as determined by differential mercury intrusion.

[00106] A twelfth embodiment which is the composition of any preceding embodiment wherein the distance between the first maximum of the first peak and the second maximum of the second peak is at least about 400 nm.

[00107] A thirteenth embodiment which is the composition of any preceding embodiment wherein the first peak is non-Gaussian and has a peak width at half height that is greater than the peak width at half height of the second peak.

[00108] A fourteenth embodiment which is the composition of any preceding embodiment wherein the support has a crush strength of from about 1 lbf to about 50 lbf.

[00109] A fifteenth embodiment which is the composition of any preceding embodiment wherein the support has an attrition of from about 0.05% to about 5%.

[00110] A sixteenth embodiment which the composition of the second embodiment wherein the sphere has a diameter of from about 1 mm to about 10 mm.

[00111] A seventeenth embodiment which is the composition of any preceding embodiment further comprising a halide.

[00112] An eighteenth embodiment which is the composition of any preceding embodiment further comprising a Group 10 metal.

[00113] A nineteenth embodiment which is the composition of any preceding embodiment further comprising a Group 1B metal.

[00114] A twentieth embodiment which is the composition of any preceding embodiment further comprising chloride.

[00115] A twenty-first embodiment which is a method of preparing a hydrogenation catalyst comprising shaping a mixture comprising a high surface area alumina, a pore former, and water to form a shaped support, wherein the shaped support comprises a low angularity particle shape; drying the shaped support to form a dried support; calcining the dried support to form a calcined support; contacting the calcined support with a chlorine-containing compound to form a chlorided support; reducing the amount of chloride in the chlorided support to form a cleaned support; and contacting the cleaned support with a Group 10 metal and a Group 1B metal to form a hydrogenation catalyst, wherein a pore size distribution for the hydrogenation catalyst displays at least two peaks of pore diameters, each peak having a maximum, wherein a first peak has a first maximum of pore diameters that is equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters that is less than about 200 nm.

[00116] A twenty-second embodiment which is the method of the twenty-first embodiment wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has a surface area of from about 1 m²/g to about 35 m²/g.

[00117] A twenty-third embodiment which is the method of any of the twenty-first through twenty-second embodiments wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has a total pore volume of from about 0.1 cc/g to about 0.9 cc/g as determined by mercury intrusion.

[00118] A twenty-fourth embodiment which is the method of any of the twenty-first through twenty-third embodiments wherein the shaped support is a sphere or a refined extrudate.

[00119] A twenty-fifth embodiment which is the method of the twenty-fourth embodiment wherein the sphere has a diameter of from about 1 mm to about 10 mm.

[00120] A twenty-sixth embodiment which is the method of any of the twenty-first through twenty-fifth embodiments wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has a crush strength of from about 1 lbf to about 50 lbf.

[00121] A twenty-seventh embodiment which is the method of any of the twenty-first through twenty-sixth embodiments wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has an attrition of from about 0.05% to about 5%.

[00122] A twenty-eighth embodiment which is the method of any of the twenty-first through twenty-seventh embodiments wherein greater than or equal to about 5% of a total pore volume of the hydrogenation catalyst is contained within the first peak of pore diameters.

[00123] A twenty-ninth embodiment which is the method of any of the twenty-first through twenty-eighth embodiments wherein the high surface area alumina comprises activated alumina, gamma alumina, rho alumina, boehmite, psuedoboehmite, bayerite or combinations thereof.

[00124] A thirtieth embodiment which is the method of any of the twenty-first through twenty-eighth embodiments wherein the high surface area alumina consists essentially of activated alumina and/or gamma alumina.

[00125] A thirty-first embodiment which is a low angularity particle shape support formed from a high surface area alumina, wherein a pore size distribution for the low angularity particle shape support displays at least two peaks of pore diameters, each peak having a maximum; wherein a first peak has a first maximum of pore diameters of equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters of less than about 200 nm; wherein greater than or equal to about 15% of a total pore volume of the low angularity particle shape support is contained within the first peak of pore diameters; and wherein the low angularity particle shape support is a sphere or a refined extrudate and has an attrition of from about 0.05% to about 5%.

[00126] A thirty-second embodiment which is a method of preparing a hydrogenation catalyst comprising selecting an inorganic material having a multimodal distribution of pore diameters, wherein at least one distribution of pore diameters comprises pores having a diameter of equal to or greater than about 200 nm; shaping a mixture comprising the inorganic material and water to form

a shaped support wherein the shaped support has a low angularity particle shape and an attrition of from about 0.05% to about 5%; drying the shaped support to form a dried support; calcining the dried support to form a calcined support; and contacting the calcined support with a Group VIII metal and a Group 1B metal to form a hydrogenation catalyst.

[00127] A thirty-third embodiment which is the method of the thirty-second embodiment further comprising contacting the calcined support with a chlorine-containing compound to form a chlorided support; contacting the chlorided support with a wash solution to form a washed support; contacting the washed support with the Group VIII metal and the Group 1B metal to form the hydrogenation catalyst.

[00128] A thirty-fourth embodiment which is the method of any of the thirty-second through thirty-third embodiments wherein the inorganic material comprises a high surface area alumina

[00129] A thirty-fifth embodiment which is the method of the thirty-fourth embodiment wherein the high surface area alumina comprises activated alumina, gamma alumina, rho alumina, boehmite, pseudoboehmite, bayerite or combinations thereof.

[00130] A thirty-sixth embodiment which is the method of the thirty-fourth embodiment wherein the high surface area alumina consists essentially of activated alumina and/or gamma alumina.

[00131] A thirty-seventh embodiment which is a method for selectively hydrogenating a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon in an olefin rich hydrocarbon stream comprising introducing into a reactor a hydrocarbon fluid stream comprising a highly unsaturated hydrocarbon in the presence of hydrogen and a catalyst composition under conditions effective to convert the highly unsaturated hydrocarbon to a less unsaturated hydrocarbon, wherein at least 50% of the catalyst composition comprises the hydrogenation catalyst produced according to the method of the thirty-second embodiment.

[00132] A thirty-eighth embodiment which is a method comprising preparing a plurality of low angularity particle shaped supports consisting essentially of α -alumina formed from a high surface area alumina, wherein the low angularity shaped supports have an attrition of from about 0.05% to about 5%; plotting the pore diameter as a function of a log of differential mercury intrusion for the low angularity particle shaped supports; and identifying the low angularity particle shaped supports having at least two peaks, each peak having a maximum, wherein a first peak comprises pores with a first pore diameter maximum equal to or greater than about 200 nm, and wherein the first peak of

pore diameters represents greater than or equal to about 5% of a total pore volume of the low angularity particle shaped supports.

[00133] A thirty-ninth embodiment which is the method of the thirty-eighth embodiment further comprising marketing the low angularity particle shaped supports for use in preparing a selective hydrogenation catalyst.

[00134] A fortieth embodiment which is a hydrogenation catalyst comprising a Group 10 metal, a Group 1B metal and at least one of the identified low angularity particle shaped supports of the thirty-eighth embodiment.

[00135] A forty-first embodiment which is a packaged product comprising at least one of the identified low angularity particle shaped supports of the thirty-eighth embodiment and written material describing use of the identified low angularity particle shaped supports in the preparation of hydrogenation catalysts having a reduced fouling rate.

[00136] While 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, etc.). 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, etc.

[00137] 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 embodiments of the present invention. The disclosures of all patents, patent applications, and

publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A composition comprising:
a support formed from a high surface area alumina and having a low angularity particle shape; and
at least one catalytically active metal,
wherein the support has pores, a total pore volume, and a pore size distribution; wherein the pore size distribution displays at least two peaks of pore diameters, each peak having a maximum; wherein a first peak has a first maximum of pore diameters of equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters of less than about 200 nm; and wherein greater than or equal to about 5% of a total pore volume of the support is contained within the first peak of pore diameters.
2. The composition of claim 1 wherein the low angularity particle shape is a sphere.
3. The composition of claim 1 wherein the low angularity particle shape is a refined extrudate.
4. The composition of any preceding claim wherein the high surface area alumina comprises activated alumina, gamma alumina, rho alumina, boehmite, psuedoboehmite, bayerite or combinations thereof.
5. The composition of any of claims 1-3 wherein the high surface area alumina consists essentially of activated alumina and/or gamma alumina.
6. The composition of any preceding claim wherein the first maximum of the first peak of pore diameters is from about 200 nm to about 9000 nm.
7. The composition of any preceding claim wherein greater than or equal to about 10% of the total pore volume of the support is contained within the first peak of pore diameters.
8. The composition of any preceding claim wherein the first maximum of the first peak of pore diameters is from about 400 nm to about 8000 nm.
9. The composition of any preceding claim wherein greater than or equal to about 15% of the total pore volume of the support is contained within the first peak of pore diameters.
10. The composition of any preceding claim having a surface area of from about 1 m²/g to about 35 m²/g.

11. The composition of any preceding claim having a total pore volume of from about 0.1 cc/g to about 0.9 cc/g as determined by differential mercury intrusion.
12. The composition of any preceding claim wherein the distance between the first maximum of the first peak and the second maximum of the second peak is at least about 400 nm.
13. The composition of any preceding claim wherein the first peak is non-Gaussian and has a peak width at half height that is greater than the peak width at half height of the second peak.
14. The composition of any preceding claim wherein the support has a crush strength of from about 1 lbf to about 50 lbf.
15. The composition of any preceding claim wherein the support has an attrition of from about 0.05% to about 5%.
16. The composition of claim 2 wherein the sphere has a diameter of from about 1 mm to about 10 mm.
17. The composition of any preceding claim further comprising a halide.
18. The composition of any preceding claim further comprising a Group 10 metal.
19. The composition of any preceding claim further comprising a Group 1B metal.
20. The composition of any preceding claim further comprising chloride.
21. A method of preparing a hydrogenation catalyst comprising:
 - shaping a mixture comprising a high surface area alumina, a pore former, and water to form a shaped support, wherein the shaped support comprises a low angularity particle shape;
 - drying the shaped support to form a dried support;
 - calcining the dried support to form a calcined support;
 - contacting the calcined support with a chlorine-containing compound to form a chlorided support;
 - reducing the amount of chloride in the chlorided support to form a cleaned support; and
 - contacting the cleaned support with a Group 10 metal and a Group 1B metal to form a hydrogenation catalyst,wherein a pore size distribution for the hydrogenation catalyst displays at least two peaks of pore diameters, each peak having a maximum, wherein a first peak has a first maximum of pore diameters that is equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters that is less than about 200 nm.

22. The method of claim 21 wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has a surface area of from about 1 m²/g to about 35 m²/g.
23. The method of claim 21 or 22 wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has a total pore volume of from about 0.1 cc/g to about 0.9 cc/g as determined by mercury intrusion.
24. The method of claim 21, 22, or 23 wherein the shaped support is a sphere or a refined extrudate.
25. The method of claim 24 wherein the sphere has a diameter of from about 1 mm to about 10 mm.
26. The method of any of claims 21 through 25 wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has a crush strength of from about 1 lbf to about 50 lbf.
27. The method of any of claims 21 through 26 wherein the calcined support, the chlorided support, the cleaned support, or the hydrogenation catalyst has an attrition of from about 0.05% to about 5%.
28. The method of any of claims 21 through 27 wherein greater than or equal to about 5% of a total pore volume of the hydrogenation catalyst is contained within the first peak of pore diameters.
29. The method of any of claims 21 through 28 wherein the high surface area alumina comprises activated alumina, gamma alumina, rho alumina, boehmite, psuedoboehmite, bayerite or combinations thereof.
30. The method of any of claims 21 through 29 wherein the high surface area alumina consists essentially of activated alumina and/or gamma alumina.
31. A low angularity particle shape support formed from a high surface area alumina, wherein a pore size distribution for the low angularity particle shape support displays at least two peaks of pore diameters, each peak having a maximum; wherein a first peak has a first maximum of pore diameters of equal to or greater than about 200 nm and a second peak has a second maximum of pore diameters of less than about 200 nm; wherein greater than or equal to about 15% of a total pore volume of the low angularity particle shape support is contained within the first peak of pore diameters; and wherein the low angularity particle

- shape support is a sphere or a refined extrudate and has an attrition of from about 0.05% to about 5%.
32. A method of preparing a hydrogenation catalyst comprising:
- selecting an inorganic material having a multimodal distribution of pore diameters, wherein at least one distribution of pore diameters comprises pores having a diameter of equal to or greater than about 200 nm;
 - shaping a mixture comprising the inorganic material and water to form a shaped support wherein the shaped support has a low angularity particle shape and an attrition of from about 0.05% to about 5%;
 - drying the shaped support to form a dried support;
 - calcining the dried support to form a calcined support; and
 - contacting the calcined support with a Group VIII metal and a Group 1B metal to form a hydrogenation catalyst.
33. The method of claim 32 further comprising contacting the calcined support with a chlorine-containing compound to form a chlorided support; contacting the chlorided support with a wash solution to form a washed support; contacting the washed support with the Group VIII metal and the Group 1B metal to form the hydrogenation catalyst.
34. The method of claim 32 or 33 wherein the inorganic material comprises a high surface area alumina.
35. The method of claim 34 wherein the high surface area alumina comprises activated alumina, gamma alumina, rho alumina, boehmite, psuedoboehmite, bayerite or combinations thereof.
36. The method of claims 35 wherein the high surface area alumina consists essentially of activated alumina and/or gamma alumina.
37. A method for selectively hydrogenating a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon in an olefin rich hydrocarbon stream comprising introducing into a reactor a hydrocarbon fluid stream comprising a highly unsaturated hydrocarbon in the presence of hydrogen and a catalyst composition under conditions effective to convert the highly unsaturated hydrocarbon to a less unsaturated hydrocarbon, wherein at least 50% of the catalyst composition comprises the hydrogenation catalyst produced according to claim 32.

38. A method comprising:
preparing a plurality of low angularity particle shaped supports consisting essentially of α -alumina formed from a high surface area alumina, wherein the low angularity shaped supports have an attrition of from about 0.05% to about 5%;
plotting the pore diameter as a function of a log of differential mercury intrusion for the low angularity particle shaped supports; and
identifying the low angularity particle shaped supports having at least two peaks, each peak having a maximum, wherein a first peak comprises pores with a first pore diameter maximum equal to or greater than about 200 nm, and wherein the first peak of pore diameters represents greater than or equal to about 5% of a total pore volume of the low angularity particle shaped supports.
39. The method of claim 38 further comprising marketing the low angularity particle shaped supports for use in preparing a selective hydrogenation catalyst.
40. A hydrogenation catalyst comprising a Group 10 metal, a Group 1B metal and at least one of the identified low angularity particle shaped supports of claim 38.
41. A packaged product comprising at least one of the identified low angularity particle shaped supports of claim 38 and written material describing use of the identified low angularity particle shaped supports in the preparation of hydrogenation catalysts having a reduced fouling rate.