

SELECTIVE HYDROGENATION CATALYST HAVING A MIXED ALUMINA PHASE SUPPORT

[0001] The present disclosure relates to a catalyst composition that includes bi-metallic nanoparticles contained on a carrier and a method of making the catalyst composition. The catalyst composition is useful in the selective hydrogenation of highly unsaturated hydrocarbons contained in a treatment stream of less unsaturated hydrocarbons.

BACKGROUND

[0002] Steam crackers and refinery cracking units provide for production of unsaturated hydrocarbon product streams that are used as feedstocks for downstream processes and in other applications. Steam crackers typically crack lower molecular weight saturated hydrocarbons, such as ethane, propane, and butane, or naphtha boiling range hydrocarbons to yield lighter alkenes, such as ethylene, propylene, and butylene. Refinery cracking units typically crack heavier hydrocarbon fractions to yield multiple product streams among which are lighter gaseous hydrocarbons having high concentrations of unsaturated hydrocarbons.

[0003] One problem with the light olefin product streams yielded from these cracking units is that the olefin product streams may contain unacceptable concentrations of more highly unsaturated hydrocarbons (e.g., diolefins, alkynes, aromatics, etc.). For example, an ethylene product stream may have a contaminating concentration of acetylene, or a propylene product stream may have contaminating concentrations of methylacetylene (MA) and propadiene (PD). The acetylene contained in the ethylene product stream, and the methylacetylene and propadiene contained in the propylene product stream need to be removed from these product streams for them to be useable.

[0004] Thus, the highly unsaturated hydrocarbons such as diolefins and hydrocarbons having triple bonds (alkynes) need to be removed from the less unsaturated product streams such as ethylene or propylene product streams. Selective hydrogenation processes typically are used to remove undesired highly unsaturated hydrocarbons (e.g., alkenes, alkynes, etc.) from less unsaturated hydrocarbon streams (e.g., ethylene and propylene).

[0005] The selective hydrogenation process is a catalytic process. This process includes contacting under suitable reaction conditions an olefin stream having a concentration of more highly unsaturated hydrocarbons with a selective hydrogenation catalyst. The more highly

unsaturated hydrocarbons are selectively hydrogenated to olefins with a minimal amount of hydrogenation of the desirable olefins (e.g., ethylene and/or propylene) of the olefin streams. Desirable characteristics of the selective hydrogenation catalyst is that it has high activity for providing the described selective hydrogenation and it exhibits a long operating life.

[0006] PCT publication, WO 2013/186789, describes one of these selective hydrogenation catalysts. This catalyst comprises an inorganic oxide carrier and so-called fine-alloy particles of an active metal component and a promoter component. The active metal is selected from palladium, platinum, and nickel, and the promoter is selected from silver, gold, and copper. The fine-alloy particles are dispersed onto the surface of the inorganic oxide carrier by a con-current dispersion process, which employs an equilibrium absorption impregnation of the inorganic oxide carrier by contacting it with a solution comprising the fine alloy particles. The inorganic carrier used in this catalyst includes alpha alumina, theta alumina, delta alumina, gamma alumina, and combinations thereof. However, there is no disclosure regarding the ratio or amounts of the different phases of alumina in the inorganic carrier.

BRIEF SUMMARY

[0007] In one embodiment, a method of making a selective hydrogenation catalyst includes forming a mixed phase alumina support having a BET surface area in the range of between approximately 30 to approximately 60 square meters/gram (m^2/g). The mixed phase alumina support includes alpha alumina and theta alumina. The method also includes impregnating the mixed phase alumina support with an impregnation solution having one or more metals selected from Group VIIIB, Group IB, or both of the Periodic Table of Elements to form an impregnated support, drying the impregnated support at a temperature in the range of between approximately 100 degrees Celsius ($^{\circ}\text{C}$) and 150 $^{\circ}\text{C}$ to form a dried impregnated support, calcining the dried impregnated support at a temperature range of between 350 $^{\circ}\text{C}$ and approximately 500 $^{\circ}\text{C}$ to form a calcined impregnated support, and reducing the one or more metals on the calcined impregnated support at a temperature in the range of between approximately 400 $^{\circ}\text{C}$ and approximately 600 $^{\circ}\text{C}$ in the presence of hydrogen to form the selective hydrogenation catalyst.

[0008] In another embodiment, a selective hydrogenation catalyst, including a mixed phase alumina support having a BET surface area in the range of between approximately 30 to

approximately 60 square meters/gram (m^2/g) and having alpha alumina and theta alumina. The alpha alumina is present in an amount of between 30 vol.% and 70 vol.% and the balance is theta alumina. The selective hydrogenation catalyst also includes bimetallic nanoparticles having at least one metal selected from Group VIII B and at least one metal selected from Group IB of the Periodic Table of Elements.

[0009] In a further embodiment, a method for the selective hydrogenation of acetylene, including contacting a selective hydrogenation catalyst with an olefin stream having a contaminating concentration of unsaturated hydrocarbons under selective hydrogenation reaction conditions. The selective hydrogenation catalyst includes a mixed phase alumina support having a BET surface area in the range of between approximately 30 to approximately 60 square meters/gram (m^2/g) and having alpha alumina and theta alumina, the alpha alumina is present in an amount of between 30 vol.% and 70 vol.% and the balance is theta alumina, and bimetallic nanoparticles having at least one metal selected from Group VIII B of the Periodic Table and a promoting metal from Group IB.

[0010] Additional features and advantages of exemplary implementations of the disclosure will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by the practice of such exemplary implementations. The features and advantages of such implementations may be realized and obtained by means of the instruments and combinations particularly pointed out in the appended claims. These and other features will become more fully apparent from the following description and appended claims or may be learned by the practice of such exemplary implementations as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Advantages of the disclosure may become apparent upon reading the following detailed description and upon reference to the drawings in which:

[0012] FIG. 1 is a flow diagram of a method of making a selective hydrogenation catalyst having a mixed phase alumina support in which the mixed phase alumina support is impregnated in one step, in accordance with an embodiment of the present disclosure;

[0013] FIG. 2 is a flow diagram of a method of making a selective hydrogenation catalyst having a mixed phase alumina support having a two-step impregnation process, in accordance with an embodiment of the present disclosure;

[0014] FIG. 3 is a plot of catalyst selectivity/reactor temperature as a function of time for the catalytic performance of an inventive catalyst and a comparative catalyst, in accordance with an embodiment of the present disclosure;

[0015] FIG. 4 is a plot of mass of green oil (GO) as a function of time on stream for the inventive catalyst and comparative catalyst, in accordance with an embodiment of the present disclosure; and

[0016] FIG. 5 is a bar graph of an amount of GO trapped in a cooling trap during a selective hydrogenation process when using the inventive catalyst and the comparative catalyst, in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

[0017] One or more specific embodiments of the present disclosure will be described below. These described embodiments are examples of the presently disclosed techniques. Additionally, in an effort to provide a concise description of these embodiments, not all features of an actual implementation may be described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions will be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure.

[0018] When introducing elements of various embodiments of the present disclosure, the articles "a," "an," and "the" are intended to mean that there are one or more of the elements. The terms "comprising," "including," and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements. Additionally, it should be understood that references to "one embodiment" or "an embodiment" of the present disclosure are not intended to

be interpreted as excluding the existence of additional embodiments that also incorporate the recited features.

[0019] The terms “approximately,” “about,” and “substantially” as used herein represent an amount close to the stated amount that still performs a desired function or achieves a desired result. For example, the terms “approximately,” “about,” and “substantially” may refer to an amount that is within less than 10% of, within less than 5% of, within less than 1% of, within less than 0.1% of, and within less than 0.01% of a stated amount.

[0020] As discussed above, selective hydrogenation for the removal of unsaturated hydrocarbons such as acetylene, methylacetylene, and propadiene, is a catalytic process. In certain existing catalysts used for the selective hydrogenation of unsaturated hydrocarbons, the hydrogenation activity decreases over time due to aging. For example, during selective hydrogenation, undesirable side products (e.g., heavy waxes and green oil) resulting from the hydrogenation of the unsaturated hydrocarbons form and buildup on the catalyst surfaces. The buildup of these undesirable side products over time cause catalyst aging and deactivation, thereby decreasing the overall performance of the selective hydrogenation catalyst. Therefore, it would be advantageous to develop a selective hydrogenation catalyst for removing unsaturated hydrocarbons from olefin streams that mitigates formation of undesirable side products and has improved performance and stability compared to existing catalysts.

[0021] Selective hydrogenation catalysts are generally supported catalyst having one or more noble/precious metals (e.g., platinum, palladium, gold, silver, etc.). For example, the selective hydrogenation catalyst may include a support (or carrier) having one or more noble metals such as palladium (Pd) with a promoting amount of silver (Ag) impregnated onto the support. The supports used in existing catalysts are alumina based and have a BET surface area less than or equal to approximately 20 square meters/gram (m^2/g). These alumina base supports are made up of mostly alpha alumina. For example, the alumina based supports of existing catalysts may have greater than 90% alpha alumina. However, as discussed above, during selective hydrogenation of olefin streams having a large amount of unsaturated hydrocarbons (e.g., greater than approximately 1 volume % (vol. %)) undesirable side products form that result in aging of the catalyst and decreased performance. As such, reaction temperatures are increased such that a desired amount of selective conversion of the unsaturated hydrocarbons to smaller unsaturated C_2 and/or C_3

hydrocarbons may be achieved. It has been surprisingly found that, by using a support having mixed phase alumina, formation of the undesirable side products is decreased. As such catalyst aging may be mitigated and desired catalyst performance is maintained. For example, as discussed in further detail below, the selective hydrogenation catalyst of the present disclosure includes a support having a mixture of theta (θ) alumina and alpha (α) alumina, which mitigates formation of undesirable side products (e.g., waxes and gas oils) during the selective hydrogenation process and improves the overall performance of the catalyst.

[0022] In addition to the selective hydrogenation catalyst, the present disclosure includes contacting under suitable reaction conditions an olefin process stream, which may have a concentration of highly unsaturated hydrocarbons (e.g., unsaturated hydrocarbons), with the catalyst. The catalyst provides for selective hydrogenation of the highly unsaturated hydrocarbons (e.g., unsaturated hydrocarbons having 6 or more carbon atoms) to less unsaturated hydrocarbons, i.e., olefins, but with a minimum amount (e.g., less than 5%) of undesirable hydrogenation of the olefins of the olefin process stream. Indeed, when referring in this specification to the selective hydrogenation catalyst disclosed herein, what is meant is that the catalyst provides for the hydrogenation of highly unsaturated hydrocarbons, such as alkynes and polyolefins, contained in the olefin stream without hydrogenating a significant amount of olefins (e.g., alkenes) in the olefin stream to saturated hydrocarbons (e.g., alkanes).

[0023] The disclosed catalyst is highly selective, particularly, when used in the selective hydrogenation of acetylene contained in ethylene process streams. The catalyst is also very stable in that the rate of decline in its selectivity and activity with time-on-stream (TOS) is much lower than that of other comparative catalysts. For example, the disclosed catalyst has a rate of decline in its selectivity and activity with TOS that is approximately 5 to 6 times lower compared to existing catalysts. This means that the cycle length of the catalyst in use is much longer than the cycle length for other comparative catalysts. In fact, the catalyst disclosed herein can provide for a cycle length more than twice that for other catalysts.

[0024] The unexpectedly high selectivity characteristic of the disclosed catalyst provides for a much lower yield (e.g., less than approximately 50%) of undesirable unsaturated C₄₊ hydrocarbons and/or green oil by-product when the catalyst is used in the selective hydrogenation process. The term “green oil” as used herein refers to a mixture of compounds produced by side reactions during

the selective hydrogenation of alkynes and diolefins contained in the olefin process stream. These side reactions form dimers, trimers and other oligomers of the alkynes and diolefins. The green oil oligomer compounds can have up to 24 or more carbon atoms per molecule.

[0025] The disclosed catalyst composition is a selective hydrogenation catalyst or selective hydrogenation catalyst precursor that can provide the numerous benefits discussed herein. This composition includes a mixed alumina phase support/carrier that contains impregnated bi-metallic nanoparticles. The bi-metallic nanoparticles include one or more noble metal components such as, for example, a silver component and a palladium component. These bi-metallic nanoparticles have a silver-enriched outer surface.

[0026] The alumina support used to prepare the catalyst composition disclosed herein significantly contributes to its special properties. For example, existing selective hydrogenation catalysts have a support that is made up of greater than 90% alpha alumina and a surface area of below 20 m²/g BET surface. In contrast, the support of the selective hydrogenation catalyst of the present disclosure has equal to or less than approximately 70% alpha alumina. In particular, the disclosed catalyst has between approximately 30% to approximately 70% alpha alumina. In addition to the alpha alumina, the support also has theta alumina. The theta alumina is present in an amount of between approximately 30% and approximately 70%. For example, in embodiments in which the alpha alumina in the support is 70%, the theta alumina makes up 30% of the total alumina in the support. In one embodiment, the ratio of alpha-to-theta alumina in the support is 1:1. In this particular example, the alpha alumina and the theta alumina each make up 50% of the total alumina in the support.

[0027] As discussed above, the surface area of the support in existing selective hydrogenation catalyst is less than approximately 20 m²/g BET surface. However, unlike the existing catalysts, the surface area of the support used in the catalyst disclosed herein has between approximately 30-60 m²/g BET surface. The surface area of the mixed phase alumina support is impacted by the ratio of alpha-to-theta alumina. It has been found that by having in the range of approximately 30% and approximately 70% theta alumina, the desired surface area of the mixed phase alumina may be achieved.

[0028] By using the mixed phase alumina support in the selective hydrogenation catalysts disclosed herein, aging of the catalysts may be mitigated and the overall performance improved compared to existing catalysts. For example, as discussed in further detail below, the selective hydrogenation catalyst of the present disclosure results in less formation of heavy even numbered carbon side products (e.g., C₆, C₈, C₁₀₊), which may form heavy waxes and green oil that build up on catalyst surfaces and undesirably impact performance.

[0029] In addition to the mixed phase alumina support, there are other characteristics of the selective hydrogenation catalyst disclosed herein that contribute to its unexpected properties and performance. Among these is the relative amounts of noble metals (e.g., silver and palladium metals) contained in the catalyst. The ratio of, for example, silver and palladium, may be an important contributor to the selectivity of the catalyst. In all instances, the palladium-to-silver molar ratio of the bi-metallic nanoparticles should be within the range of from 0.01:1 to 1:10. However, it may be desirable for the silver and palladium to be present such that the palladium-to-silver molar ratio is within a much narrower range. Particularly, in certain embodiments, the molar ratio of palladium-to-silver in the bi-metallic nanoparticles is in the range of from 1:6.

[0030] The bi-metallic nanoparticles have an overall diameter of less than or equal to approximately 4 nanometers (nm). For example, the bi-metallic nanoparticles may have an overall diameter of 1, 2, 3, or 4 nm. As should be appreciated, not all the bi-metallic nanoparticles on the support have a diameter of 4 nm. The bi-metallic nanoparticles on any given support may have different diameters within a desired range. In a preferred embodiment, the bi-metallic nanoparticles have an overall diameter in the range of approximately 2 nm and approximately 3 nm.

[0031] With the foregoing in mind, **FIG. 1** is a block diagram of a method **10** for preparing the selective hydrogenation catalyst disclosed herein. The method **10** includes forming a mixed phase alumina support (block **12**). For example, to form the mixed phase alumina support, an alumina precursor is placed in a calciner (e.g., a rotary calciner or the like) and calcined at a temperature of between approximately 1000 degrees Celsius (°C) and approximately 1200 °C for between approximately 2 hours to approximately 6 hours, thereby forming the mixed phase alumina support. In a preferred embodiment, the alumina precursor is calcined at a temperature between 1075 °C and 1100 °C for 3 to 5 hours. The alumina precursor may be mixed of boehmite, gamma

alumina, theta alumina, alpha alumina, gibbsite, diaspora or any other suitable alumina that results in an alumina mixture having both alpha and theta phases. The alumina precursor may be any suitable size and shape. For example, the alumina precursor may be in the form of tablets, pellets, extrudates, or any other suitable shape, and have a size between 0.5 millimeter (mm) and 20 mm.

[0032] Calcining the alumina precursor at temperatures above 1000 °C transforms the phase of the alumina precursor into different phases. In particular, the phase of the alumina precursor is transformed into alpha and theta phase. The resultant mixed phase alumina support disclosed herein has between approximately 30 weight % (wt%) and approximately 70 wt% alpha alumina and the balance is theta alumina. For example, in one embodiment, the mixed phase alumina support has 30 wt% alpha alumina and 70 wt% theta alumina. In other embodiments, the mixed phase alumina support has 70 wt% alpha alumina and 30 wt% theta alumina. In a preferred embodiment, the mixed phase alumina support has 50 wt% alpha alumina and 50 wt% theta alumina. The amount of alpha and theta alumina in the resultant mixed phase alumina support may be controlled by the calcination temperature and the duration of calcination.

[0033] The alumina precursor may be formed into a desired shaped structure by any known suitable method. Extruded shaped structures typically are prepared by mixing the desired alumina powder with water and one or more additives to form a mixture having plastic properties and forming the mixture into extrudates by any of the known extrusion methods. The formed extrudates may be cylinders, lobed-shaped, and twisted shapes having nominal extrudate diameters in the range of from 0.5 mm to 25 mm and extrudate lengths in the range of from 1 mm to 50 mm.

[0034] Spherically shaped structures or balls of the alumina precursor may be made by the application of any of the known granulation methods, which use an inclined rotating disk or pan that is fed particles of the inorganic oxide while spraying a cohesive slurry onto the particles. By this method the particles are formed into spherically shaped particles. The spherically shaped carrier particles have diameters in the range of from 0.5 mm to 25 mm.

[0035] Dry tableting methods may also be used to prepare the shaped alumina precursor structure. In this method, cylindrical pellets or pills of the alumina precursor are made by pressing a dry alumina powder that is optionally mixed with additives such as a lubricant and a binder, between two punches in a tableting press. Alumina precursor particles that are cylindrical pellets have

pellet diameters in the range of from 0.5 mm to 25 mm and pellet lengths in the range of from 1 mm to 50 mm. The shaped alumina precursor is calcined, as discussed above.

[0036] The shaped alumina precursor that has been calcined has a surface area and pore volume that allow for the impregnation of the mixed phase alumina support with metallic nanoparticles or metal salt solutions. The mixed phase alumina support of the present disclosure has a surface area (determined by the BET method employing N₂, ASTM test method D3037) that is in the range of from 30 m²/g to 70 m²/g, preferably, from 40 m²/g to 60 m²/g, and, most preferably, 50 m²/g, and a bulk density of in the range of from 0.7 to 0.8 grams/cubic centimeter (g/cc). It has been found that the surface area of the shaped alumina precursor may be adjusted based on an amount of the theta alumina present in the mixed phase alumina support. In particular, it has been found that by having in the range of approximately 30% to 70% theta alumina, the surface area of the mixed phase support may be increased by two to three times more than supports having alpha alumina as the only alumina phase. The higher surface area of the mixed phase alumina support compared to alumina supports of existing catalysts provides improved hydrogenation activity due, in part, to the increased metal surface area of the overall catalyst of the present disclosure.

[0037] The mixed phase alumina support resulting from the acts of block **12** has a bimodal pore size distribution with a pore radius in the range of from approximately 5 nanometers (nm) to 150 nm. The pore volume of the mixed phase alumina support is in the range of from 0.40 cubic centimeters/gram (cc/g) to 0.65 cc/g. Preferably, the pore volume is in the range of from 50 cc/g to 55 cc/g. The references herein to pore size distribution and pore volume of the calcined shaped particle are to those properties as determined by mercury intrusion porosimetry, ASTM test method D 4284. The measurement of the pore size distribution of the calcined shaped particle is by any suitable measurement instrument using a contact angle of 140° with a mercury surface tension of 474 dyne/cm at 25 °C.

[0038] The method **10** also includes preparing a metal salt impregnation solution (block **16**). The metal salt impregnation solution may be prepared by any suitable technique. For example, the metal salt may be dissolved in a desired volume of water. The metal salts used to prepare the impregnation solution(s) include, but are not limited to, noble metal salts such as a palladium salt and a silver salt. By way of non-limiting example, the palladium salt used in the preparation of the impregnation solution is selected from the group of palladium salts consisting of palladium

nitrate, palladium halide, palladium carbonate, palladium phosphate, palladium acetate, palladium oxide and palladium sulfate, and the silver salt used in the preparation of the impregnation solution is selected from the group of silver salts consisting of silver nitrate, silver halide, silver carbonate, silver phosphate, silver acetate, silver hydroxide, silver oxide, and silver sulfate.. The preferred palladium salt is palladium nitrate and the preferred silver salt is silver nitrate.

[0039] The amount of water used to dissolve the noble metal salts is such that it is equal to the pore volume of the mixed phase alumina support (so called incipient wetness). The relative amounts of the palladium salt and silver salt in the impregnation solution(s) are such that the catalyst of the present disclosure has approximately 0.01 wt% and 0.1 wt% palladium and approximately 0.03 wt% to 0.5 wt% silver.

[0040] Following preparation of the impregnation solution(s) according to the acts of block **16**, the method **10** includes impregnating the mixed phase alumina support with the impregnation solution to form an impregnated support (block **18**). For example, the impregnation solution may be sprayed onto the mixed phase alumina support at ambient temperature in a manner that the pores of the mixed phase alumina support are filled by the first impregnation solution. However, any other suitable impregnation technique may be used such as, for example, incipient wetness impregnation and wet impregnation.

[0041] The method **10** also includes drying and calcining the impregnated support to form a calcined impregnated support (block **20**). For example, the impregnated support is dried in air at a temperature of between approximately 100 °C and approximately 150 °C for 5 to 30 minutes. The resultant dried support is further calcined in air at a temperature between approximately 350 °C and approximately 500 °C for 1 to 5 hours, thereby forming the calcined impregnated support.

[0042] Following drying and calcining of the impregnated support in accordance with block **20**, the noble metals in the calcined impregnated support are reduced to form the selective hydrogenation catalyst (block **24**). For example, the calcined impregnated support is thermally treated at a temperature of between approximately 400 °C and approximately 600 °C for 1 to 6 hours in a hydrogen containing atmosphere. The hydrogen containing atmosphere may have greater than 20% hydrogen with the balance being nitrogen. In a preferred embodiment, the calcined impregnated support is thermally treated at a temperature of 500 °C. By reducing the

noble metals at temperatures in the range of approximately 400 °C and approximately 500 °C, the bimetallic nanoparticles may have a silver-enriched outer surface. The silver-enriched outer surface of the bimetallic nanoparticles is beneficial for the stability and activity of the selective hydrogenation catalyst of the present disclosure.

[0043] FIG. 2 is a flow diagram of a method 30 that may also be used to prepare the selective hydrogenation catalyst of the present disclosure. In the method 30, the mixed alumina support is prepared (block 12) in the same manner as in the method 10. However, rather than impregnating the mixed alumina support with a single impregnation solution containing both the palladium and silver salts, the method 30 separately impregnates the palladium salt and the silver salt. For example, the method 30 includes preparing a first impregnation solution and a second impregnation solution (block 32). The impregnation solutions may be prepared by dissolving a metal salt in a desired volume of water. The metal salts used to prepare the respective impregnation solutions include, but are not limited to, palladium salt and a silver salt. By way of non-limiting example, the palladium salt used in the preparation of the first impregnation solution is selected from the group of palladium salts consisting of palladium nitrate, palladium halide, palladium carbonate, palladium phosphate, palladium acetate, palladium oxide and palladium sulfate. The preferred palladium salt is palladium nitrate. The silver salt used in the preparation of the second impregnation solution is selected from the group of silver salts consisting of silver nitrate, silver halide, silver carbonate, silver phosphate, silver acetate, silver hydroxide, silver oxide, and silver sulfate. The preferred silver salt is silver nitrate.

[0044] Following preparation of the impregnation solution(s) according to the acts of block 32, the method 30 includes impregnating the mixed phase alumina support with the first impregnation solution to form a first impregnated support (block 36), drying and calcining the first impregnated support to form a first calcined impregnated support (block 38), and reducing the calcined impregnated support to form a reduced metal impregnated support (block 40). The acts of blocks 36, 38, and 40 are performed in a manner similar to the acts of blocks 18, 20, and 24, respectively.

[0045] The method 30 further includes impregnating the reduced metal impregnated support with the second impregnation solution to form a second impregnated support (block 42). Similar to the acts of block 18 of the method 10, the second impregnation solution may be sprayed onto the

reduced metal impregnated support at ambient temperature in a manner that the second impregnation solution coats the reduced metal particles within the pores of the reduced metal impregnated support. The noble metal salt in the second impregnation solution may be either the palladium salt or the silver salt depending on which noble metal is desired to be the outmost metal. In a preferred embodiment, the metal salt in the second impregnation solution is the silver salt.

[0046] The second impregnation support is dried to remove water and calcined to form a second calcined impregnated support (block 48) and the remaining second metal salt on the second calcined impregnated support is reduced (block 50) in a manner similar to the acts of blocks 20 and 24, respectively, thereby forming the selective hydrogenation catalyst of the present disclosure.

[0047] The selective hydrogenation catalyst composition of the present disclosure has a total silver content in the range of from 0.03 wt.% to 0.5 wt.% and total palladium content in the range of from 0.01 wt.% to 1 wt.%. Preferably, the total silver content is in the range of from 0.04 wt.% to 0.3 wt.%. Preferably, the total palladium content of the selective hydrogenation catalyst composition is in the range of from 0.015 wt.% to 0.09 wt.%, and, more preferably, from 0.02 wt.% to 0.08 wt.%. The weight percent silver is based on the total weight of the catalyst composition assuming the silver is metal regardless of its actual form. The weight percent palladium is based on the total weight of the catalyst composition assuming the palladium is metal regardless of its actual form.

[0048] As discussed above, the selective hydrogenation catalyst of the present disclosure may be used in the selective hydrogenation of acetylene and other highly unsaturated hydrocarbons. It has been surprising found that selective hydrogenation catalysts having a mixed phase alumina support in combination with a surface area greater than 20 m²/g, such as the catalyst of the present disclosure, decrease the formation of undesirable side products that cause catalyst aging and undesirably impact performance. Therefore, due, at least in part, to the decrease in undesirable side products, the disclosed catalyst is more stable and the overall performance is improved compared to existing catalysts. The selective hydrogenation process may be carried out in a single reactor or more than one reactor connected in any suitable flow arrangement. If more than one reactor is employed, then the reactors may be arranged in parallel flow or series flow or a combination of the two flow arrangements. Each reactor defines a reaction zone that contains a

volume of the selective hydrogenation catalyst. The reactors are each equipped with a feed inlet means for receiving and introducing a feed stream into its reaction zone, which is operated at selective hydrogenation reaction conditions. The reactors are also each equipped with a reactor effluent outlet means for withdrawing a reactor effluent from its reaction zone.

[0049] In the selective hydrogenation process, an olefin feed is introduced into a reaction zone containing the selective hydrogenation catalyst disclosed herein. The olefin feed is an alkene product stream, which includes monounsaturated hydrocarbons, and contacted with the catalyst within the reaction zone under selective hydrogenation reaction conditions. The preferred monounsaturated hydrocarbon product streams may be a product stream of either ethylene, propylene, or butylene, or a combination of these low-molecular weight olefins.

[0050] The olefin feed or alkene product stream treated by the selective hydrogen process of the present disclosure can also contain a contaminating concentration of highly unsaturated hydrocarbons, such as an alkyne, e.g., acetylene or methylacetylene, and polyunsaturated hydrocarbons, such as diolefins, e.g., propadiene. The selective hydrogenation catalyst disclosed herein provides for the selective hydrogenation of the highly unsaturated hydrocarbons contained in the olefin feed to their respective monosaturated hydrocarbon, i.e. olefin, with a minimum amount of hydrogenation of the olefins of the olefin feed to saturated hydrocarbons (e.g., ethane).

[0051] The preferred use of the selective hydrogenation catalyst is in the selective hydrogenation of acetylene contained in an ethylene product stream or the selective hydrogenation of methylacetylene and propadiene contained in a propylene product stream. Of these two processes, the selective hydrogenation catalyst of the present disclosure is particularly useful in the selective hydrogenation of acetylene contained in an ethylene product stream.

[0052] The ethylene product feed to the selective acetylene hydrogenation process can typically have an acetylene concentration exceeding 100 parts per million mole (ppmm) to 2 mole %. The selective hydrogenation process can reduce the concentration of acetylene contained in the ethylene product feed to yield a reactor effluent or treated ethylene product having a reduced concentration of acetylene typically having a concentration significantly below 100 ppmm. This process is highly selective in the hydrogenation of acetylene. The selectivity is typically greater than 70%. More typically, the selectivity is greater than 72%, and even greater than 74%. The

ethylene selectivity is defined as the volume of ethylene in the reactor outlet effluent less the volume of ethylene in the reactor inlet feed divided by the difference of acetylene in the reactor inlet feed and acetylene in the reactor outlet effluent multiplied by 100. The selective hydrogenation of acetylene to ethylene is usually carried out as a gas-phase process at a space velocity of the gaseous ethylene stream of from 500 v/vh to 15,000 v/vh, based on the catalyst volume, a temperature in the range of from 10 °C to 250 °C, and a pressure of from 0.01 bar to 90 bar. The molar ratio of hydrogen to acetylene in the feed that is contacted with the selective hydrogenation catalyst is typically in the range of from 0.8 to 1.8.

[0053] The selective hydrogenation of methylacetylene and propadiene contained in propylene streams to form propylene can be carried out as a gas-phase process or a liquid phase process. For the gas phase process, typically, the space velocity of the propylene stream ranges from 1,500 v/vh to 5,000 v/vh, based on the catalyst volume. Reaction temperatures may range from 50 °C to 180 °C and pressures from 10 bar to 35 bar. The molar ratio of hydrogen to methylacetylene and propadiene in the propylene stream in the feed that is contacted with the selective hydrogenation catalyst is typically in the range of from 0.8 to 2.

[0054] The following examples are provided to illustrate the unexpected and improved performance of the selective hydrogenation catalyst of the present disclosure, but they should not be construed as limiting it in any way. For each sample, the depth of deposited precious metals on the catalysts was determined using an Electron probe microanalyzer (EPMA). The EPMA uses an electron beam coupled with wavelength-dispersive x-ray spectrometers (WDX) to provide information on the chemical composition of the surface of a sample. A cross section of the catalyst is prepared by polishing the sample. Point measurements in predefined positions (usually in 50 µm steps) along the cross section are done by movement of the motorized sample stage under a nonmoving electron beam. This resulting in a line scan of various dots. The impregnation thickness can then be determined through the concentrations along the positions on the line over the cross section.

Example 1 – one step impregnation

[0055] This Example 1 describes the preparation of Catalyst 1 that is representative of the inventive catalyst.

[0056] 5 mm tablets of gamma alumina are calcined at a temperature of approximately 1100 °C for 3 to 5 hours to form a mixed phase alumina support having 50% alpha alumina and 50% theta alumina. An impregnating solution is made by dissolving an amount of palladium nitrate ($\text{Pd}(\text{NO}_3)_2$) and silver nitrate (AgNO_3) in a volume of water that is equal to the pore volume of the mixed phase alumina support that yields approximately 0.03% Pd and 0.18% Ag on the final catalyst. At ambient temperature, the impregnating solution is sprayed onto the mixed phase alumina support. The impregnated mixed alumina phase support is dried in air for 2 hours at a temperature of 120 °C. The dried impregnated mixed phase alumina support is calcined in air for 3 hours at a temperature 500 °C. Once calcined, the resultant impregnated mixed phase alumina carrier is heated at 400 °C for 1 hour in a hydrogen-containing atmosphere having >20% hydrogen to reduce the palladium and silver metals and form the selective hydrogenation catalyst 1. The resultant Catalyst 1 has 95% of the Pd metal deposited in the outer 100 micrometers (μm) of the mixed alumina phase support.

Example 2 – two-step impregnation

[0057] This Example 2 describes the preparation of Catalyst 2 that is representative of the inventive catalyst.

[0058] 5 mm tablets of gamma alumina are calcined at a temperature of approximately 1100 °C for 3 to 5 hours to form a mixed phase alumina support having 50% alpha alumina and 50% theta alumina. A palladium (Pd) impregnating solution is made by dissolving palladium nitrate ($\text{Pd}(\text{NO}_3)_2$) in a volume of water that is equal to the pore volume of the mixed phase alumina support. The amount of $\text{Pd}(\text{NO}_3)_2$ dissolved in the water is such that it yields approximately 0.03 wt% Pd. Similarly, a silver (Ag) impregnating solution is made by dissolving AgNO_3 in a volume of water that is equal to the pore volume of the mixed phase alumina support. The amount of AgNO_3 dissolved in the volume of water is such that it yields approximately 0.18 wt% Ag on the final catalyst. At ambient temperature, the Pd impregnating solution is sprayed onto the mixed phase alumina support. The Pd impregnated mixed alumina phase support is dried in air for 2 hours at a temperature of 120 °C. The dried Pd impregnated mixed phase alumina support is calcined in air for 3 hours at a temperature 500 °C. Once calcined, the resultant Pd impregnated mixed phase alumina carrier is heated at 150 °C for 1 hour in a hydrogen-containing atmosphere having >20% hydrogen to reduce the palladium metal.

[0059] Following reduction of the palladium metal, the Pd impregnated mixed phase alumina support is impregnated with the Ag impregnating solution at ambient temperature. The Pd and Ag impregnated mixed phase alumina support is dried in air for 2 hours at a temperature of 120 °C. The dried Pd impregnated mixed phase alumina support is calcined in air for 3 hours at a temperature 500 °C. Once calcined, the resultant Pd and Ag impregnated mixed phase alumina carrier is heated at 400 °C for 1 hour in a hydrogen-containing atmosphere having >20% hydrogen to reduce the palladium metal. The resultant Catalyst 2 has 95% of the Pd and Ag metals deposited in the outer 200 micrometers (μm) of the mixed alumina phase support.

Example 3 - comparative

[0060] This Example 3 describes the preparation of Catalyst 3 that is representative of the comparative catalyst.

[0061] 400 grams (g) of 4x4 mm tablets of an alpha aluminum oxide support was impregnated with an 2% hydrazine aqueous solution. The volume of the hydrazine aqueous solution was equivalent to 35% of the pore volume of the alpha aluminum oxide support. An aqueous solution of $\text{Pd}(\text{NO}_3)_2$ and AgNO_3 was prepared such that a yield of Pd content and Ag content in the catalyst was 0.035 wt% and 0.025 wt%, respectively. The support was impregnated with a volume of the Pd and Ag aqueous solution equivalent to 65% of the pore volume of the support. The resultant impregnated support was dried and calcined at 630 °C for 5 hours under a nitrogen atmosphere to obtain the comparative catalyst.

[0062] Table 1 below provides properties of the selective hydrogenation catalysts of Examples 1-3 above.

Table 1. Properties of Inventive and Comparative Selective Hydrogenation Catalysts

		INVENTIVE CATALYST 1	INVENTIVE CATALYST 2	COMPARATIVE
BET Surface Area (m^2/g)		50	50	14
Al_2O_3	α	50	50	95
Phases (%)	θ	50	50	5
Pd (wt%)		0.03	0.03	0.035
Ag (wt%)		0.18	0.18	0.025

Example 4

[0063] This Example 4 describes the performance testing done to characterize the catalyst compositions of Examples 1 and 3.

[0064] Experimental conditions were chosen which closely resemble those of a first tail-end reactor of a steam cracker unit.

[0065] A laboratory reactor was filled with 15 cc of catalyst in five layers, diluted by 85 cc of α -alumina spheres. A feed having the composition presented in Table 2 was fed to the reactor at a rate providing a GHSV of 4,000 v/vh. The reactor was operated at a pressure of 10 bar and a temperature that was adjusted and maintained to provide at least 55% conversion of the acetylene, i.e., a 9,000 ppm acetylene concentration at the reactor outlet.

Table. 2. Reactor Feed Composition

Feed Components	Vol. %
C ₂ H ₂ (acetylene)	2.0
H ₂	2.0
C ₂ H ₄ (ethylene)	30
N ₂	Balance

[0066] FIG. 3 illustrates a plot 54 of selectivity and stability of the selective hydrogenation catalyst of Example 1 compared to that of Example 3. As shown in the plot 54, selectivity data 56 and reactor temperature 58 when using the Catalyst 1 of the present disclosure illustrates the improved stability and selectivity of the catalyst when used for hydrogenation of acetylene for over 400 hours on stream compared to the comparative catalyst. The inventive Catalyst 1 maintained a selectivity to ethylene of greater than 70% after 450 hours. Moreover, the reactor temperature 58 did not require increasing to maintain greater than 55% acetylene conversion after 450 hours. In contrast, as shown by selectivity and temperature data 60, 62, respectively, the selectivity of the comparative Catalyst 3 decreased and dropped below 70% after approximately 100 hours and even after the reactor temperature was increased to maintain at least 55% conversion, the selectivity of the comparative Catalyst 3 did not improve. Instead, the selectivity 60 of the comparative Catalyst 3 continued to decrease. Therefore, based on the data presented in plot 54, the inventive Catalyst

1 provides a significantly better acetylene conversion selectivity to ethylene than the comparative Catalyst 3. As such, the ethylene yield is higher for the Catalyst 1 compared to the comparative Catalyst 3. The selectivity of the catalysts is calculated as follows: $[(\text{ethylene outlet concentration} - \text{ethylene inlet concentration}) / (\text{acetylene inlet concentration} - \text{acetylene outlet concentration})] * 100$.

[0067] Moreover, rather than increasing the temperature 58 to maintain 55% conversion in tests using the Catalyst 1, the temperature 58 was decreased. In sharp contrast, the temperature 62 used in testing of the comparative Catalyst 3 was increased after 100 hours and continued to be increased to maintain 55% conversion. After 200 hours, the comparative Catalyst 3 was unable to maintain 55% conversion even after increasing the temperature.

[0068] Another measure of the improved acetylene conversion selectivity to ethylene for the catalyst of the present disclosure is the amount of green oil produced during the hydrogenation process. Green oil is a mixture of hydrocarbons having greater than 8 carbon atoms (C_{8+}) that condense under the hydrogenation reaction conditions. The green oil may condense on the pores of the catalyst and the reactor. Condensation of the green oil on and within the pores of the catalyst undesirably impact the performance of the catalyst. That is, the green oil contributes to catalyst aging and decreases acetylene conversion selectivity to ethylene. FIGS. 4 and 5 illustrate a plot 68 and bar graph 70 of the green oil produced over time during the hydrogenation process and collected on the catalyst and within a cold trap, respectively. As shown in FIG. 4, the comparative Catalyst 3 produced over 1 g of green oil at 300 hours and continued to increase to 1.5 at 600 hours, whereas the Catalyst 1 produced less than approximately 0.6 g at 300 hours. Moreover, as shown in FIG. 5, the Catalyst 1 has less green oil accumulated on its surface compared to the comparative Catalyst 3 and less green oil was collected in the cold trap when the Catalyst 1 was used over the comparative Catalyst 3. Therefore, a yield of green oil is lower when using the catalyst of the present disclosure over the comparative catalyst.

[0069] The technical effects of using a mixed phase alumina support for selective hydrogenation catalysts improves the overall performance of these catalyst for the selective conversion of highly unsaturated hydrocarbons (e.g., alkynes, alkadienes, etc.) into less unsaturated hydrocarbons such as ethylene and propylene. The mixed phase alumina support used in these catalysts have both alpha and theta alumina in a desired ratio that increases the BET surface area of the support by 2

to 3 times compared to existing selective hydrogenation catalysts, which generally have alpha phase only alumina supports. In particular, the mixed phase alumina support has in the range of approximately 30% and 70% theta alumina, the balance being alpha alumina. The combination of the theta alumina, the increased surface area, and bimodal pore size distribution of the catalyst of the present disclosure provides an improvement in the selective hydrogenation of acetylene and other highly unsaturated olefins for conversion into ethylene and other less saturated olefins.

[0070] The present disclosure may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the disclosure is, therefore, indicated by the appended claims rather than by the foregoing description. All changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

We claim:

1. A method of making a selective hydrogenation catalyst, comprises:
 - forming a mixed phase alumina support having a BET surface area in the range of between approximately 30 to approximately 60 square meters/gram (m^2/g), wherein the mixed phase alumina support comprises alpha alumina and theta alumina;
 - impregnating the mixed phase alumina support with an impregnation solution comprising one or more metals selected from Group VIIIB, Group IB, or both of the Periodic Table of Elements to form an impregnated support;
 - drying the impregnated support at a temperature in the range of between approximately 100 degrees Celsius ($^{\circ}\text{C}$) and 250 $^{\circ}\text{C}$ to form a dried impregnated support;
 - calcining the dried impregnated support at a temperature range of between 350 $^{\circ}\text{C}$ and approximately 550 $^{\circ}\text{C}$ to form a calcined impregnated support; and
 - reducing the one or more metals on the calcined impregnated support at a temperature in the range of between approximately 350 $^{\circ}\text{C}$ and approximately 650 $^{\circ}\text{C}$ in the presence of hydrogen to form the selective hydrogenation catalyst.
2. The method according to claim 1, wherein forming the mixed phase alumina support comprises calcining an alumina precursor at a temperature in the range of between approximately 1075 $^{\circ}\text{C}$ and approximately 1100 $^{\circ}\text{C}$, wherein the alumina precursor comprises boehmite or gamma alumina.
3. The method according to claims 1 and 2, wherein the mixed phase alumina has between 30% and 70% alpha alumina and the balance is theta alumina.
4. The method according to any one of the preceding claims, wherein a ratio of alpha alumina to theta alumina is 1:1.
5. The method according to any one of the preceding claims, wherein the one or more metals selected from Group VIIIB is palladium and the one or more metals selected from Group IB is silver, and wherein the palladium and the silver metals are in the form of a metal salt.

6. The method according to any one of the preceding claims, wherein impregnating the mixed phase alumina comprises a first impregnation step to impregnate the mixed phase alumina support with a first impregnation solution comprising palladium nitrate or a silver nitrate to form a first impregnated support and a second impregnation step to impregnate the first impregnated support with a second impregnation solution different from the first impregnation solutions to form a second impregnated support, wherein the first impregnation solution and the second impregnation solutions comprise palladium nitrate or silver nitrate, wherein the first impregnated support is dried, calcined and reduced before the second impregnation step to form a reduced impregnated support, and wherein the second impregnated support is dried, calcined, and reduced after the second impregnated step to form the catalyst.
7. The method according to any one of the preceding claims, wherein approximately 95% of at least one metal is within a depth of 100 micrometers (μm) of the catalyst, and wherein the depth extends from an outermost surface of the mixed phase alumina support and toward an innermost surface of the mixed phase alumina support.
8. A selective hydrogenation catalyst, comprising:
a mixed phase alumina support having a BET surface area in the range of between approximately 30 to approximately 60 square meters/gram (m^2/g) and comprising alpha alumina and theta alumina, wherein the alpha alumina is present in an amount of between 30 vol.% and 70 vol.% and the balance is theta alumina; and
bimetallic nanoparticles comprising at least one metal selected from Group VIIIB and at least one metal selected from Group IB of the Periodic Table of Elements.
9. The catalyst according to claim 8, wherein a ratio of alpha alumina to theta alumina is 1:1.
10. The catalyst according to claims 8 and 9, wherein the amount of alpha alumina and theta alumina is 50 vol.%.

11. The catalyst according to any one of the preceding claims, comprising a bulk density of in the range of approximately 0.7 grams/cubic centimeter (g/cc) and approximately 0.8 g/cc.
12. The catalyst according to any one of the preceding claims, wherein 95% of the bimetallic nanoparticles are within a depth of 100 micrometers (μm) of the catalyst, and wherein the depth extends from an outermost surface of the mixed phase alumina support and toward an innermost surface of the mixed phase alumina support.
13. The catalyst according to any one of the preceding claims, wherein the at least one metal selected from Group VIIIB is palladium and the at least one metal selected from Group IB is silver.
14. A method for the selective hydrogenation of acetylene, comprising:
contacting an olefin stream having a contaminating concentration of unsaturated hydrocarbons under selective hydrogenation reaction conditions with the selective hydrogenation catalyst according to any one of claims 8 to 13.