CONVENTION

AUSTRALIA
Patents Act 1990

REQUEST FOR A STANDARD PATENT
AND NOTICE OF ENTITLEMENT

The Applicant identified below requests the grant of a patent to the nominated person identified below for an invention described in the accompanying standard complete patent specification.

Applicant and Nominated Person:
Phillips Petroleum Company
Bartlesville, Oklahoma 74004, UNITED STATES OF AMERICA

Invention Title:
CATALYST COMPOSITION USEFUL FOR HYDROGENATING UNSATURATED HYDROCARBONS

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Details of basic application(s):
08/740,527 UNITED STATES OF AMERICA US 30 October 1996

Applicant states the following:
1. The nominated person is the assignee of the actual inventors.
2. The nominated person is the assignee of the applicants of the basic application.
3. The basic application was the first made in a convention country in respect of the invention.

The nominated person is not an opponent or eligible person described in Section 33-3b of the Act.

26 August 1997
Phillips Petroleum Company
By PHILLIPS ORMONDE & FITZPATRICK
Patent Attorneys for the Applicant
By

Our Ref : 501918
5999q

David B Fitzpatrick
A composition and a process for using the composition in a selective hydrogenation of a highly unsaturated hydrocarbon such as, for example, an alkyne or diolefin, to a less unsaturated hydrocarbon such as, for example, an alkene or a monoolefin, are disclosed. The composition comprising palladium, silver, and a spinel wherein the palladium and silver are each present in a sufficient amount to effect the selective hydrogenation of an unsaturated hydrocarbon. Optionally, the palladium is present as skin distributed on the surface of the spinel. The composition can further comprise an alkali metal-containing compound such as, for example, potassium fluoride.
The following statement is a full description of this invention, including the best method of performing it known to applicant(s):
FIELD OF THE INVENTION

This invention relates to a composition and a process useful for catalytically hydrogenating an unsaturated hydrocarbon compound.

BACKGROUND OF THE INVENTION

It is well known to one skilled in the art that an unsaturated hydrocarbon compound can be produced by a thermal cracking process. For example, a fluid stream containing a saturated hydrocarbon such as, for example, ethane, propane, butane, pentane, naphtha, or combinations of any two or more thereof can be fed into a thermal (or pyrolytic) cracking furnace. Within the furnace, the saturated hydrocarbon is converted to an unsaturated hydrocarbon compound such as, for example, ethylene and propylene. Unsaturated hydrocarbons are an important class of chemicals that find a variety of industrial uses. For example, ethylene can be used as a monomer or comonomer for producing a polyolefin. Other uses of unsaturated hydrocarbons are well known to one skilled in the art.

However, an unsaturated hydrocarbon produced by a thermal cracking process generally contains an appreciable amount of less desirable alkyne(s) or diolefin(s). For example, ethylene produced by thermal cracking of ethane is generally contaminated with some acetylene which must be selectively hydrogenated to ethylene, but not to ethane, in a hydrogenation reaction.

The selective hydrogenation of alkynes is generally, commercially carried out in the presence of an alumina-supported palladium catalyst. In the case of the selective hydrogenation of acetylene to ethylene, a palladium and silver catalyst supported on an alumina can be employed. See for example, U.S. Patent No. 4,404,124 and U.S. Patent No. 4,484,015, disclosures of which are herein incorporated by reference. The operating temperature for this hydrogenation process is selected such that essentially all alkyne, such as, for example, acetylene is hydrogenated to its corresponding alkene such as, for example, ethylene thereby removing the alkyne from the product stream while only an insignificant amount of alkene is hydrogenated to alkane. Such a selective hydrogenation process minimizes the losses of desired unsaturated hydrocarbons, and, in the front-end and total cracked gas processes, avoids a "runaway" reaction which is difficult to control, as has been pointed out in the above-identified patents.
It is generally known to those skilled in the art that impurities such as carbon monoxide, H₂S, COS, mercaptans and organic sulfides which are present in an alkyne-containing feed or product stream can poison and deactivate a palladium-containing catalyst. For example, carbon monoxide is well known to temporarily poison or inactivate such a hydrogenation catalyst thereby making the selective hydrogenation less effective.

A palladium-containing "skin" catalyst in which palladium is distributed on the surface or "skin" of the catalyst has been developed which is known to be more selective and active than a non-skin catalyst in converting acetylene in an ethylene stream to ethylene. See for example, U.S. Patent No. 4,484,015, disclosure of which is incorporated herein by reference. It is well known that the catalyst selectivity is determined, in part, by the skin thickness. Generally, catalyst selectivity decreases as the skin thickness increases. There is therefore an ever-increasing need to develop a catalyst having a better "skin" on the catalyst for a better selective hydrogenation of an alkyne to an alkene.

Palladium supported on alumina has been successfully used in dry hydrogenation processes for many years. However, in some processes such as the so-called "total cracked gas" process in which the steam is not removed from the olefins stream, the selective hydrogenation of an alkyne to alkene must be accomplished in the presence of steam. In such processes, the alumina supported catalyst may have a much shorter life because alumina is not stable in steam. Therefore, there is also an increasing need to develop a palladium catalyst on a steam-stable support.

As such, development of an improved palladium catalyst and a process therewith in the selective hydrogenation of an alkyne to an alkene in the presence of an impurity would be a significant contribution to the art and to the economy.

**SUMMARY OF THE INVENTION**

It is an object of this invention to provide a composition that can be used for selectively hydrogenating an alkyne to an alkene. It is another object of this invention to provide a palladium-containing catalyst composition wherein the palladium is better distributed on the skin of the composition, as compared to known "skin" catalysts. It is also an object of this invention to provide a process for selectivity
hydrogenating an alkyne to its corresponding alkene in the presence of an impurity. It is a further object of this invention to carry out a selective hydrogenation of acetylene to ethylene in the presence of an impurity. Other objects and advantages will become more apparent as this invention is more fully described hereinbelow.

According to a first embodiment of this invention, a composition which can be used for selectively hydrogenating a highly unsaturated hydrocarbon such as, for example, an alkyne or a diolefin, is provided. The composition comprises palladium, silver, and a spinel such as a metal aluminate or a metal titanate wherein the metal of the spinel is selected from the group consisting of zinc, magnesium, iron, manganese, any metal that can form a spinel structure, such as Zr, Mo, Ru, Rh, Co, Ge, Ca, and combinations of any two or more thereof.

According to a second embodiment of this invention, a process which can be used for selectively hydrogenating a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon is provided. The process comprises contacting a highly unsaturated hydrocarbon with hydrogen, in the presence of a catalyst composition, under a condition sufficient to effect a selective hydrogenation of the highly unsaturated hydrocarbon. The catalyst composition can be the same as the composition disclosed in the first embodiment of this invention.

DETAILED DESCRIPTION OF THE INVENTION

As used in the present invention, the term "fluid" denotes gas, liquid, or combination thereof. The term "saturated hydrocarbon" is referred to as any hydrocarbon which can be converted to an unsaturated hydrocarbon such as an olefinic compound by a thermal cracking process. An "unsaturated hydrocarbon" as used in this application is a hydrocarbon having at least one double bond between carbon atoms in the molecule. Generally, example of saturated hydrocarbons include, but are not limited to, ethane, propane, butanes, pentanes, hexanes, octanes, decanes, naphtha, and combinations of any two or more thereof. Examples of unsaturated hydrocarbons include, but are not limited to, monoolefins such as ethylene, propylene, butenes, pentenes, hexenes, octenes, and decenes; aromatic compounds such as naphthalene; alkynes such as acetylene, propyne, and butynes; diolefins such as butadienes, pentadienes (including isoprene), hexadienes, octadienes, and decadienes; and combinations of two or more thereof. The term "highly unsaturated hydrocarbon"
refers to a hydrocarbon which contains a triple bond or two or more double bonds in a molecule. The term "less unsaturated hydrocarbon" refers to a hydrocarbon in which the triple bond in the high unsaturated hydrocarbon is hydrogenated to a double bond or a hydrocarbon in which the number of double bonds is one less than that in the highly unsaturated hydrocarbon. The term "selective hydrogenation" is referred to as a hydrogenation process which converts a highly unsaturated hydrocarbon such as an alkyne or a diolefin to a less unsaturated hydrocarbon such as a monoolefin without hydrogenating the less unsaturated hydrocarbon to a saturated or a more saturated hydrocarbon such as alkane.

According to the first embodiment of this invention, a composition which can be used to selectively hydrogenate an alkyne or a diolefin to monoolefin is provided. The composition can comprise, consist essentially of, or consists of palladium, silver, and a spinel such as, for example, a metal aluminate or a metal titanate wherein the palladium can be present on the skin of the composition and the silver can be distributed on the skin of or throughout the composition, and the metal of the spinel is the same as that disclosed above. The presently preferred spinel is zinc aluminate, zinc titanate, magnesium aluminate, or combinations of any two or more thereof. These spinels are readily available and effective. The term "skin" is referred to as the surface of the composition. The "skin" can be any thickness as long as such thickness can promote the selective hydrogenation disclosed herein. Generally, the thickness of the skin can be in the range of from about 1 to about 1000, preferably about 5 to about 500, more preferably about 5 to about 250, and most preferably 10 to 100 µm. Presently, it is preferred that palladium and silver are supported on the spinel.

Generally, palladium can be present in the composition in any weight percent (%) so long as the palladium is substantially concentrated on the skin of the composition and the weight % is effective to selectively hydrogenate an alkyne to an alkene, or a diolefin to a monoolefin. The weight % of palladium can be in the range of from about 0.0001 to about 3, preferably about 0.0005 to about 1.5, and most preferably 0.001 to 1.0%. Similarly, silver can be present in the composition in any weight % as long as the weight % can effect the selective hydrogenation of an alkyne to an alkene, or a diolefin to a monoolefin. Generally, silver can be present in the composition in the range of from about 0.0003 to about 20, preferably about 0.003 to
about 10, and most preferably 0.003 to 5 weight %. Optionally, the composition can
also comprise, consist essentially of, or consist of palladium, silver, an alkali metal or
alkali metal-containing compound, and a spinel such as a metal titanate or a metal
aluminate. The alkali metal or alkali metal-containing compound can be present in the
composition in any weight % that can effect the selective hydrogenation of an alkyne to
an alkene, or a diolefin to a monoolefin, and in the range of from about 0.001 to about
10, preferably about 0.005 to about 5, and most preferably about 0.01 to about 2
weight %. The presently preferred alkali metal compound is an alkali metal fluoride
such as, for example, potassium fluoride. Generally, the spinel can make up the rest of
the composition.

The composition can be in any physical form and dimension so long as the
physical form and dimension can be used as a catalyst for selectively hydrogenating
an alkyne to an alkene, or a diolefin to a monoolefin. Generally, it is preferred the
physical form be spherical or cylindrical for such form is easy to handle. The
composition generally has a size in the range of from about 0.1 to about 20, preferably
about 0.5 to about 15, and most preferably 1 to 10 mm in diameter. The composition
can have a surface area of from about 0.1 to about 50, preferably about 0.5 to about
10 m²/g, as determined by the well-known BET method employing nitrogen.

Generally, any spinel can be used in the composition so long as the
composition can effect the selective hydrogenation of an alkyne to an alkene, or a
diolefin to a monoolefin. As disclosed above, the metal of the spinel can include
magnesium, zinc, iron, manganese, any metal that can form a spinel, and combinations
of any two or more thereof. Examples of suitable spinels include, but are not limited
to, zinc aluminate, magnesium aluminate, zinc titanate, calcium aluminate, manganese
aluminate, ferrous aluminate, calcium titanate, magnesium titanate, and combinations of
any two or more thereof.

The composition can be prepared by any suitable techniques. Generally,
the palladium can be placed on a spinel in any suitable manner that will yield a
composition meeting the above-described parameters. The presently preferred
technique involves impregnating a spinel with an aqueous solution of a suitable
palladium compound. Generally, the extent of penetration of the palladium can be
controlled by adjustment of the acidity of the solution with an acid such as, for
example, hydrochloric acid.

Examples of suitable palladium compounds include, but are not limited to, palladium chloride, palladium bromide, palladium iodide, palladium acetate, palladium nitrate, palladium sulfate, palladium sulfide, palladium acetylacetonate, and combinations of any two or more thereof. The presently preferred palladium compound is palladium chloride for it is readily available.

One can use any suitable method to determine whether substantial weight percent of the composition particles have the palladium concentrated in an area within certain distance of the exterior surface. One technique currently favored is the electron microprobe which is well known to one skilled in the art. Another technique involves breaking open a representative sample of calcined catalyst pills and treating them with a dilute alcoholic solution of N,N-dimethyl-para-nitrosoaniline. The treating solution reacts with the oxidized palladium to give a red color which can be used to evaluate the distribution of the palladium. Still another technique involves breaking open a representative sample of calcined catalyst pills followed by treatment with a reducing agent such as, for example, hydrogen to change the color of the skin.

The silver can be distributed on the skin of or throughout the composition in any suitable and effective manner. Examples of suitable silver compounds include, but are not limited to, silver chloride, silver bromide, silver iodide, silver acetate, silver nitrate, silver sulfate, silver fluoride, silver perchloride, and combinations of any two or more thereof. It is currently preferred to employ an aqueous silver nitrate solution in a quantity greater than that necessary to fill the pore volume of the composition. Generally, the weight ratio of silver to palladium can be in the range of from about 0.1:1 to about 20:1, preferably about 1:1 to about 10:1, and most preferably 3:1 to 8:1.

The impregnated composition can be dried at a temperature in the range of about 25°C. to about 150°C., preferably about 25°C. to 120°C., and most preferably 30°C. to 120°C., followed by calcining at a temperature of from about 200°C. to about 1,200°C., preferably about 275°C. to about 850°C., and most preferably 400°C. to 700°C. for about 1 to about 40 hours, preferably about 1 to about 30 hours, and most preferably 2 to 25 hours.

Any alkali metal-containing compounds can be used in the composition
if the resulting composition can effect a selective hydrogenation of an alkyne to an alkene, or a diolefin to a monoolefin. Examples of suitable alkali metal compounds include sodium fluoride, potassium fluoride, lithium fluoride, rubidium fluoride, cesium fluoride, sodium iodide, potassium iodide, lithium iodide, rubidium iodide, cesium iodide, sodium chloride, potassium chloride, lithium chloride, rubidium chloride, cesium chloride, sodium bromide, potassium bromide, lithium bromide, rubidium bromide, cesium bromide, sodium hydroxide, potassium hydroxide, lithium hydroxide, rubidium hydroxide, cesium hydroxide, sodium oxide, potassium oxide, lithium oxide, rubidium oxide, cesium oxide, sodium carbonate, potassium carbonate, lithium carbonate, rubidium carbonate, cesium carbonate, sodium nitrate, potassium nitrate, lithium nitrate, rubidium nitrate, cesium nitrate, and combinations of any two or more thereof. The presently preferred alkali metal-containing compound is potassium fluoride for it is effective in the selective hydrogenation. The alkali metal-containing compound can be incorporated into a spinel by any method known to one skilled in the art. For example, an alkali metal-containing compound can be impregnated or sprayed onto a spinel before it is impregnated with a suitable palladium compound, and preferably also with a suitable silver compound. Alternatively, the alkali metal-containing compound can be incorporated, for example, by impregnation or spraying onto the composition simultaneously with or after the impregnation with a suitable palladium compound. The alkali metal-containing compound can also be incorporated into a spinel between the palladium and silver impregnation steps or after the impregnation with palladium and silver compounds. Alternatively, one can also apply a "wet reducing" step which is a treatment with dissolved reducing agents such as hydrazine, alkali metal borohydrides, aldehydes such as formaldehyde, carboxylic acids such as formic acid or ascorbic acid, reducing sugars such as dextrose.

In the second embodiment of this invention, a process for selectively hydrogenating a highly unsaturated hydrocarbon such as, for example, an alkyne or a diolefin, to a less unsaturated hydrocarbon such as, for example, a monoolefin is provided. The process can comprise, consist essentially of, or consist of contacting a highly unsaturated hydrocarbon with hydrogen, in the presence of a catalyst under a condition sufficient to effect the selective hydrogenation of an alkyne to an alkene, or a diolefin to a monoolefin. Though any highly unsaturated hydrocarbon can be used in
the process, it is presently preferred that an alkyne or diolefin containing 2 to about 12, preferably 2 to about 10, and most preferably 2 to 6 carbon atoms be used.

The catalyst composition can be the same composition described above in the first embodiment of this invention. Hydrogen can be present either in the feed stream containing the highly unsaturated hydrocarbon or in a hydrogen-containing fluid which is mixed with the feed stream before contacting with the catalyst composition. If a hydrogen-containing fluid is used, it can be a substantially pure hydrogen or any fluid containing sufficient concentration of hydrogen to effect the hydrogenation. It can also contain other gases such as, for example, nitrogen, methane, carbon monoxide, carbon dioxide, steam, or combinations of any two or more thereof so long as the hydrogen-containing fluid contains sufficient concentration of hydrogen to effect the hydrogenation.

Optionally, the catalyst can be first treated, prior to the selective hydrogenation, with a hydrogen-containing fluid to activate the catalyst. Such reductive, or activation, treatment can be carried out at a temperature in the range of about 20°C to about 200°C, preferably about 25°C to about 150°C, and most preferably 30°C to 125°C, for a time period of about 1 minute to about 30 hours, preferably about 0.5 to about 25 hours, and most preferably 1 to 20 hours. During this reductive treatment, palladium and silver compounds (primarily oxides) which may be present in the catalyst composition after the drying step and the calcining step described above are substantially reduced to palladium and silver metal. When this optional reductive treatment is not carried out, the hydrogen gas present in the reaction medium accomplishes this reduction of oxides of palladium and silver during the initial phase of the selective hydrogenation reaction of this invention.

The selective hydrogenation process of this invention can be carried out by contacting a fluid which comprises a highly unsaturated hydrocarbon, in the presence of hydrogen, with the catalyst composition disclosed above. The highly unsaturated hydrocarbon can further comprise a fluid which can be water, steam, water containing a soluble or insoluble substance, or combinations of any two or more thereof. Preferably, the fluid containing a highly unsaturated hydrocarbon is an unsaturated alkene stream containing an alkyne, a diolefin, or both as an impurity, generally at a level of about 1 mg/Kg (ppm) to about 50,000 ppm of the fluid. The highly unsaturated hydrocarbon and the hydrogen can be in the fluid stream that is not a major component, or a diolefin include, but are not limited to, acetylene, propylene, 3-methyl-1-butyn, 1-hexyne, combinations of any two or more thereof. These alkynes are primarily hydrocarbons. acetylene is primarily hydrogen; propylene, and the butynes are the dienes and the butenes are the dienes (2-butenes). Examples of these diolefins are selectively reduced in order to best attain substantially the highly unsaturated hydrocarbon, there is 1 mole of the highly unsaturated hydrocarbon and hydrogen. A fluid containing a highly unsaturated hydrocarbon can be introduced into a reactor before their introduction to a reactor, then placed in the reactor before introduction. The process is known to one skilled in the art of the present invention. The process is batch, or continuous mode.

The term "impurities, of the fluid stream that is not a major component, a diolefin include, but are not limited to, sulfide (COS), mercaptans (RSH), methane, ethane, propane, butane, ketones, carboxylic acids, esters, two or more thereof, wherein containing 1 to about 15, preferably present in the fluid stream in
highly unsaturated hydrocarbon can be, for example, an alkyne, a diolefin, or combinations of any two or more thereof. Examples of suitable alkynes include, but are not limited to, acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and combinations of any two or more thereof. The presently preferred alkyne is acetylene. These alkynes are primarily hydrogenated to the corresponding alkenes. For example, acetylene is primarily hydrogenated to ethylene, propyne is primarily hydrogenated to propylene, and the butynes are primarily hydrogenated to the corresponding butenes (1-butene, 2-butene). Examples of suitable diolefins include, but are not limited to, butadienes, isoprene, pentadienes, cyclopentadienes, hexadienes, cyclohexadienes, octadienes, cyclooctadienes, decadienes, and combinations of any two or more thereof. These diolefins are selectively hydrogenated to their corresponding monoolefins. In order to best attain substantially complete selective hydrogenation of a highly unsaturated hydrocarbon, there should be at least about one mole of hydrogen for each mole of the highly unsaturated hydrocarbon present. A fluid containing a highly unsaturated hydrocarbon and hydrogen can be introduced into a reactor. Alternatively, a fluid containing a highly unsaturated hydrocarbon and a hydrogen-containing fluid can be introduced into a reactor separately, contemporaneously introduced, or premixed before their introduction to a reactor to contact with the catalyst which is generally laced in the reactor before introduction of the fluid(s) into the reactor. Any reactors known to one skilled in the art for selective hydrogenation can be employed in the present invention. The process of the invention can be carried out in a batch, semi-batch, or continuous mode.

The term "impurity" used herein denotes any component in a fluid stream that is not a major component. Examples of impurities other than an alkyne or a diolefin include, but are not limited to carbon monoxide, hydrogen sulfide, carbonyl sulfide (COS), mercaptans (RSH), organic sulfides (RSR), organic disulfides (RSSR), methane, ethane, propane, butane, carbon dioxide, water, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, other oxygenated compounds, and combinations of two or more thereof, wherein each R can be an alkyl or cycloalkyl or aryl group containing 1 to about 15, preferably 1 to 10 carbon atoms. Generally, each impurity is present in the fluid stream in trace amounts. For example, an impurity can be present
at a level of less than about 1 weight percent (%).

The temperature necessary for the selective hydrogenation of a highly unsaturated hydrocarbon such as, for example, an alkyne, to a less unsaturated hydrocarbon such as, for example, an alkene is any temperature that can effect the conversion of, for example, an alkyne to an alkene. It generally depends largely upon the activity and selectivity of a catalyst, the amounts of impurities in the fluid, and the desired extent of removal of impurities. Generally, a reaction temperature can be in the range of about 10°C. to about 300°C., preferably about 20 to about 250°C., and most preferably 30 to 200°C. Any suitable reaction pressure can be employed. Generally, the total pressure is in the range of about 50 to about 1,500, preferably about 75 to about 1,200, and most preferably 100 to 1,000 pounds per square inch gauge (psig).

The liquid or gas hourly space velocity of the fluid feed can also vary over a wide range. Typically, the gas space velocity can be in the range of about 10 to about 20,000 m³ of the fluid per m³ of catalyst per hour, more preferably about 50 to about 12,500 m³/hour, and most preferably 100 to 8,000 m³/hour. The liquid space velocity of the feed can be in the range of from about 0.001 to about 200, preferably about 0.01 to about 100, and most preferably 0.1 to 50 m³/m³/hour. The molar ratio of hydrogen to a highly unsaturated hydrocarbon is in the range of about 0.5:1 to about 10,000:1, preferably about 1:1 to about 5,000:1 and most preferably 1:1 to 1,000:1.

The hourly space velocity of the hydrogen-containing fluid, if separately fed to a reactor containing a selective hydrogenation catalyst, is chosen so as to provide a molar ratio of H₂ to a highly unsaturated hydrocarbon in the range of about 0.5:1 to about 10,000:1, preferably about 1:1 to about 5,000:1 and most preferably 1:1 to 1,000:1.

Regeneration of the catalyst composition can be accomplished by heating the catalyst composition in air (at a temperature which preferably does not exceed about 700°C.) so as to burn off any impurities such as, for example, organic matter and/or char that may have accumulated on the catalyst composition. Optionally, the oxidatively regenerated composition is reduced with H₂ or a suitable hydrocarbon (as has been described above) before its redeployment in the selective hydrogenation of this invention.

The following examples are presented to further illustrate this invention and are not to be construed as unduly limiting its scope.
EXAMPLE I

This example illustrates that catalyst having a better “skin” of palladium is produced by using a spinel.

The impregnating solution was prepared by dissolving 0.018 g of PdCl₂ into a small vial (about 10 ml) with 4 drops of concentrated HCl. The mixture was heated to almost dryness while the vial was being swirled. Distilled water (5 grams) was added to the vial to mix and dissolve the palladium salt to prepare a PdCl₂ solution. An aliquot (0.94 gram) of the thus-prepared PdCl₂ solution was then added to an α-alumina support (1.025 g; about 3-7 m²/g surface area and 0.22-0.32 cc/g; in 3/16 inch tablet form) which was obtained from UCI (United Catalysts Inc., Louisville, Kentucky) to form a mixture in a similar vial. The alumina support was soaked in the PdCl₂ solution for about 30 minutes at 25°C, while being swirled. Thereafter the excess liquid was decanted and the alumina having palladium supported thereon was placed in a porcelain dish about 3 inches in diameter, dried at 125°C, for 2 hours, and then calcined at 538°C in a force draft furnace for 2 hours. This was Pd/Al₂O₃ skin catalyst.

In a separate run, 1.07 gram of the above PdCl₂ solution was mixed with 1.159 gram of zinc aluminate (in 1/8 in tablet form; 7.3 m²/g surface area) which was obtained from Calsicat Catalyst Division of Mallinckrodt Specialty Chemicals Company, Erie, Pennsylvania. The mixture was then treated exactly as described above to produce a Pd/ZnAl₂O₄ skin catalyst.

Both skin catalysts were made in tablet forms and pills of the tablets were reduced with a hydrogen flow at about 150°F. until the color of the pills changed to gray-black. In the meantime, the supports were still snow-white in color. The change to gray-black color was due to the reduction of palladium oxide so that the palladium skin can be observed. Thereafter, individual tablets were split in half and the Palladium skin was visually observed. It was found that the skin on zinc aluminate was much better than the skin on alumina. The term “better” used herein refers to more concentrated on the skin and less penetration into the support.

EXAMPLE II

This example illustrates the production of a “skin” Pd/Ag/ZnAl₂O₄ catalyst.
Palladium chloride (PdCl$_2$, 0.0229 gram) was dissolved in 5 g of H$_2$O with 10 drops of concentrated HCl to form a solution in a beaker. The solution was heated to almost dryness on a hot plate. Water (9.61 g) was then added to reconstitute and prepare a PdCl$_2$ solution.

Zinc aluminate (58.63 grams, as 1/8 inch extrude) obtained from Calsicat which was similar to that disclosed in Example I was impregnated with the entire content of the reconstituted PdCl$_2$ solution. Following drying at 160°F for 16 hours, the catalyst was reduced in wet H$_2$ (hydrogen gas was saturated with water at 25°C.) for 16 hours at 380°C and then cooled to 160°C. followed by a purge of nitrogen and air for about 4 hours. The dried catalyst was then calcined in air at 380°C. for 5 hours.

A solution containing 0.1724 gram of AgNO$_3$ in 33.24 gram of water was used to soak the calcined catalyst for about 30 minutes and then dried at 180°F. 16 hours to prepare a dried, Ag-impregnated catalyst. The dried, Ag-impregnated catalyst was calcined at 200°C. for 16 hours in air and then 4 hours at 370°C. The catalyst was a Pd/Ag/ZnAl$_2$O$_4$ skin catalyst.

Twenty milliliters of the extrudates catalyst were packed into a water jacketed stainless steel reactor (1/2 inch inner diameter; 18 inches long). Thermocouples were inserted into a thermal well which ran through the center and coaxial with the reactor which was heated with an external water bath. The hydrocarbon feed used is shown in Table I. After the catalyst was treated with H$_2$ at 200 psig (90 cc/min) at room temperature (25°C.) for 16 hours, the feed at 200 psig was introduced into the reactor at 102°F. The feed rate was about 900 cc/minute. At intervals, the reactor effluent was sampled and analyzed with a gas chromatograph. The results of the test are shown in Table I.
TABLE I*

<table>
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<tr>
<th>T (°F)</th>
<th>C₂⁻/C₂</th>
<th>Acetylene</th>
<th>C₄'s</th>
<th>C₆'s</th>
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<tbody>
<tr>
<td>102</td>
<td>3.692</td>
<td>0</td>
<td>0.015</td>
<td>t</td>
</tr>
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<td>96</td>
<td>---</td>
<td>0.008</td>
<td>0.012</td>
<td>0.002</td>
</tr>
<tr>
<td>99</td>
<td>3.709</td>
<td>0.004</td>
<td>0.016</td>
<td>0.005</td>
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<td>0</td>
<td>0.015</td>
<td>0.005</td>
</tr>
<tr>
<td>122</td>
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<td>0</td>
<td>0.016</td>
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<tr>
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<td>0.015</td>
<td>0.007</td>
</tr>
<tr>
<td>161</td>
<td>2.803</td>
<td>0</td>
<td>0.012</td>
<td>0.005</td>
</tr>
</tbody>
</table>

*The feed contained 10.84 mole % ethane, 40.39 mole % ethylene, 0.238 mole % acetylene, about 0.02 mole % CO, 34.698 mole % methane, and essentially no ethers. The values shown are mole % except that C₂⁻/C₂ is molar ratio. A zero mole acetylene denotes acetylene content was less than 10 parts per million by moles. The C₂⁻ run away condition was when the effluent C₂ was at 12.84 mole % while the C₂⁻ in the effluent decreased to 38.39%.

EXAMPLE III

This comparative example illustrates a selective hydrogenation with a commercially available Pd/Ag/Al₂O₃ catalyst.

The catalyst was a commercial Pd/Ag/Al₂O₃ catalyst which contained 0.018 weight % Pd, 0.065 weight % Ag and about 99 weight % alumina. It had a BET/N₂ surface area of 3 to 5 m²/g, and had been prepared substantially in accordance with the method described in U.S. Patent No. 4,404,124 (column 4, lines 32-45), disclosure of which is herein incorporated by reference. This catalyst was provided by United Catalysts Inc. (UCI), Louisville, Kentucky.

The catalyst was used in a selective hydrogenation test which was carried out the same as that disclosed in Example II. The results are shown in Table II.
TABLE IIa

<table>
<thead>
<tr>
<th>T (°F)</th>
<th>( \frac{C_2^-}{C_2} )</th>
<th>Acetylene</th>
<th>( C_4^- )'s</th>
<th>( C_6^- )'s</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>---</td>
<td>0.093</td>
<td>0.011</td>
<td>0.006</td>
</tr>
<tr>
<td>108</td>
<td>---</td>
<td>0.050</td>
<td>0.016</td>
<td>0.008</td>
</tr>
<tr>
<td>117</td>
<td>3.696</td>
<td>0.002</td>
<td>0.017</td>
<td>0.008</td>
</tr>
<tr>
<td>119</td>
<td>3.682</td>
<td>0</td>
<td>0.019</td>
<td>0.008</td>
</tr>
<tr>
<td>138</td>
<td>3.436</td>
<td>0</td>
<td>0.019</td>
<td>0.007</td>
</tr>
<tr>
<td>151</td>
<td>3.163</td>
<td>0</td>
<td>0.017</td>
<td>0.006</td>
</tr>
<tr>
<td>160</td>
<td>2.887</td>
<td>0</td>
<td>0.015</td>
<td>0.005</td>
</tr>
</tbody>
</table>

*See Table I footnote a.

EXAMPLE IV

This example further illustrates the use of a Pd/Ag/ZnAl₂O₄ skin catalyst in a selective hydrogenation of acetylene to ethylene.

The catalyst was made with 30 grams of zinc aluminate, 30 grams of PdCl₂ solution, and 30 grams of AgNO₃ solution were employed. The PdCl₂ solution was prepared by diluting 12 grams of 0.1 g Pd/100 g solution of PdCl₂ to 60 grams with water and the AgNO₃ solution was prepared by dissolving 0.2268 grams of AgNO₃ in 60 grams of water.

An aliquot of PdCl₂ solution (30 grams) was added to zinc aluminate in a ceramic bowl to form a mixture. After 1 hour at 23°C, the solution was drained, the solid was dried at 125°C for 30 minutes, and then calcined for 2 hours at 454°C.

Thirty grams of AgNO₃ solution was then added to the calcined catalyst to form a second mixture. After 1 hour at 23°C, the solution was drained, the solid was dried at 125°C for 30 minutes, and then calcined at 454°C for 2 hours to prepare a Pd/Ag/ZnAl₂O₄ skin catalyst containing 0.02 weight % Pd, 0.12 weight % Ag, and 99.86 weight % ZnAl₂O₄.

The selective hydrogenation was carried out the same as that disclosed in
Example II except that the catalyst made in this Example was used. The results are shown in Table III.

In a separate, comparative run, a catalyst was prepared by the same procedure except that an \( \alpha \)-alumina was used in place of zinc aluminate. The thus-obtained Pd/Ag/Al\(_2\)O\(_3\) skin catalyst was used to selectively hydrogenate acetylene as disclosed in Example II. The results are shown in Table IV.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Ethane</th>
<th>Ethylene</th>
<th>Acetylene</th>
<th>C(_4)'s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed:</td>
<td>0</td>
<td>67.995</td>
<td>3480</td>
<td>0</td>
</tr>
<tr>
<td>99</td>
<td>0</td>
<td>68.249</td>
<td>663</td>
<td>417</td>
</tr>
<tr>
<td>104</td>
<td>795</td>
<td>68.077</td>
<td>134</td>
<td>514</td>
</tr>
<tr>
<td>105</td>
<td>1014</td>
<td>68.026</td>
<td>83</td>
<td>527</td>
</tr>
<tr>
<td>106</td>
<td>961</td>
<td>68.139</td>
<td>81</td>
<td>514</td>
</tr>
<tr>
<td>108</td>
<td>1276</td>
<td>68.043</td>
<td>0</td>
<td>360</td>
</tr>
<tr>
<td>109</td>
<td>1806</td>
<td>68.021</td>
<td>0</td>
<td>206</td>
</tr>
<tr>
<td>110</td>
<td>1623</td>
<td>68.021</td>
<td>0</td>
<td>509</td>
</tr>
<tr>
<td>113</td>
<td>2164</td>
<td>67.970</td>
<td>0</td>
<td>502</td>
</tr>
<tr>
<td>114</td>
<td>2287</td>
<td>67.964</td>
<td>0</td>
<td>350</td>
</tr>
<tr>
<td>121</td>
<td>3962</td>
<td>67.859</td>
<td>0</td>
<td>469</td>
</tr>
<tr>
<td>130</td>
<td>6894</td>
<td>67.547</td>
<td>0</td>
<td>441</td>
</tr>
<tr>
<td>139</td>
<td>11475</td>
<td>67.056</td>
<td>0</td>
<td>407</td>
</tr>
<tr>
<td>145</td>
<td>14943</td>
<td>66.734</td>
<td>0</td>
<td>368</td>
</tr>
<tr>
<td>153</td>
<td>21135</td>
<td>66.150</td>
<td>0</td>
<td>345</td>
</tr>
<tr>
<td>160</td>
<td>29370</td>
<td>65.304</td>
<td>0</td>
<td>322</td>
</tr>
</tbody>
</table>

\( \text{C}_2 \) runaway target wt \%=64.995 (feed - 3%). The values shown for ethylene are weight %. All other are ppm by weight. The feed was a deethanized ethylene feed containing 300 ppm CO and there was little or no heavies (>C\(_4\)) in the product stream.
The results in Table III show that a skin catalyst prepared on zinc aluminate spinel as support had very good catalyst activity because it had a low cleanup temperature of 107°F. The term "cleanup temperature" is defined as the temperature at which the acetylene concentration at the reactor exit is less than 20 ppm by weight.

The results in Table III also show that the Pd/Ag/ZnAl\(_2\)O\(_4\) skin catalyst had a high runaway temperature. The term "runaway temperature" is defined as the temperature above which uncontrollable hydrogenation of ethylene begins. The cleanup temperature is a measure of the catalyst activity; the lower the cleanup temperature is, the more active the catalyst is. The difference between the runaway temperature and the cleanup temperature is a measure of the selectivity of the catalyst; a more selectivity catalyst has a larger difference.

| TABLE IV\(^a\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Temp            | Ethane          | Ethylene        | Acetylene       | C\(_4\)\(^+\)'s |
| feed:           | 0               | 67.963          | 3372            | 0               |
| 106             | 910             | 68.047          | 289             | 356             |
| 111             | 1718            | 68.110          | 106             | 495             |
| 113             | 2001            | 67.963          | 61              | 237             |
| 114             | 2098            | 67.921          | 49              | 298             |
| 117             | 2249            | 67.924          | 56              | 338             |
| 118             | 4008            | 67.746          | 0               | 333             |
| 119             | 2856            | 67.842          | 23              | 330             |
| 129             | 8354            | 67.344          | 0               | 261             |
| 145             | 20401           | 66.128          | 0               | 225             |
| 146             | 20448           | 66.258          | 0               | 214             |
| 153             | 21855           | 66.050          | 0               | 189             |
| 160             | 40803           | 64.207          | 0               | 186             |

\(\text{See footnote a in Table III except that the C}_2\text{ runaway target was 64.963%}.\)
The results in Table III and IV show that the invention catalyst Pd/Ag/ZnAlO₄ had comparable activity and selectivity as a Pd/Ag/Al₂O₃ catalyst.

**EXAMPLE V**

This example shows a Pd/Ag/ZnTiO₃ skin catalyst and the use thereof in a selective hydrogenation of acetylene to ethylene.

The zinc titanate supported skin catalyst was prepared by the same procedure described in Example IV except that zinc titanate was used as support. The hydrogenation was carried out the same as that described in Example II. The results are shown in Table V below.

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Temp} & \text{Ethane} & \text{Ethylene} & \text{Acetylene} & \text{C}_4''\text{s} \\
\hline
\text{feed:} & 0 & 56.188 & 3035 & 174 \\
106 & 0 & 56.281 & 1163 & 401 \\
112 & 328 & 56.117 & 481 & 297 \\
133 & 1620 & 55.908 & 79 & 203 \\
137 & 1874 & 55.860 & 62 & 205 \\
143 & 2633 & 55.763 & 25 & 177 \\
146 & 12290 & 54.916 & 0 & 199 \\
150 & 3806 & 55.700 & 0 & 192 \\
156 & 20044 & 54.151 & 0 & 131 \\
156 & 5945 & 55.590 & 0 & 207 \\
161 & 6784 & 53.449 & 0 & 200 \\
170 & 9942 & 52.154 & 0 & 185 \\
200 & 45857 & 51.662 & 0 & 117 \\
\hline
\end{array}
\]

\*See footnote in Table III. However, the feed was a de-propanized ethylene stream containing 821 ppm CO.

Table V also shows that the skin catalyst Pd/Ag/ZnTiO₃ had a very good
catalyst activity, i.e., low cleanup temperature, and good selectivity, i.e., large
difference between the cleanup temperature and run-away temperature.

EXAMPLE VI

This example demonstrates that a magnesium aluminate can be used to
prepare a skin catalyst useful for selective hydrogenation of acetylene.

Thirty grams of Halder-Topsoe CAM-9L MgAl₂O₄ tablets
(about 5.1 x 5.4 mm, obtained from Halder-Topsoe, Houston, Texas, having a N₂ BET
surface area of 22 m²/g and a total pore volume of 0.21 cc/g) was cut in half with a
razor blade and washed with bottled H₂O 3 times and then dried at 85°C. for 16 hours.

A portion of the magnesium aluminate (24.943 grams) was covered with 24.943 grams
of 0.02 weight % Pd of a PdCl₂ solution for 15 minutes with swirling and stirring.
Excess solution was then poured off and blot-dried lightly followed by drying at 85°C.
for 3 hours.

The PdCl₂ solution was prepared as follows: First, 0.100 gram of PdCl₂
was weighted into a 30 ml beaker. Fifty drops of concentrated HCl solution was then
added to the beaker. The content in the beaker was heated slowly, gently on a hot
plate with swirling until almost dry. Distilled H₂O (15 ml) was added to the beaker
and the content was again heated with swirling to get all solid dissolved. The resulting
solution was transferred to a tared bottle and filtered through piece of Kimwipe paper
towel followed by rinsing the beaker into bottle 3 to 4 times. Water was added to the
bottle to make 300 grams of solution.

The dried mixture was calcined for 2 hours at 454°C. Thereafter, the cal-
cined Pd/MgAl₂O₄ was soaked in an AgNO₃ solution, which was prepared by dissolving
0.096 grams of AgNO₃ in 24.0 grams of bottled H₂O, for 1 hour with stirring every 15
minutes. Excess AgNO₃ solution was poured off. The solid was then blot dried on
paper towels, dried at 85°C. for 16 hours and then calcined at 454°C. in air for 2
hours.

The Pd/Ag/MgAl₂O₄ catalyst was then used to selectively hydrogenate
acetylene as described in Example II. The results are shown in Table VI.
Table VI demonstrates that a skin catalyst supported on magnesium-aluminate also had good activity and selectivity.

The results shown in Example II-VI are summarized in the following Table VII.
TABLE VIIa

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_1$ (°F.)</th>
<th>$T_2$ (°F.)</th>
<th>$\Delta T$ (°F.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Ag/Al$_2$O$_3^b$</td>
<td>118</td>
<td>157</td>
<td>39</td>
</tr>
<tr>
<td>Pd/Ag/ZnAl$_2$O$_4^c$</td>
<td>101</td>
<td>155</td>
<td>54</td>
</tr>
<tr>
<td>Pd/Ag/Al$_2$O$_3^d$</td>
<td>117</td>
<td>156</td>
<td>39</td>
</tr>
<tr>
<td>Pd/Ag/ZnAl$_2$O$_4^e$</td>
<td>108</td>
<td>163</td>
<td>55</td>
</tr>
<tr>
<td>Pd/Ag/ZnTiO$_3^f$</td>
<td>144</td>
<td>192</td>
<td>48</td>
</tr>
<tr>
<td>Pd/Ag/MgAl$_2$O$_4^g$</td>
<td>120</td>
<td>77</td>
<td>57</td>
</tr>
</tbody>
</table>

$^a$ $T_1$ denotes cleanup temperature, $T_2$ refers to runaway temperature, and $\Delta T$ is the difference between $T_1$ and $T_2$. The larger the $\Delta T$ is, the better the selectivity is. All data were obtained from runs with de-ethanized ethylene feed containing 300 ppm CO, except Pd/Al/ZnTiO$_3$, footnote f.

$^b$ See Table II
$^c$ See Table I.
$^d$ See Table IV.
$^e$ See Table III.
$^f$ See Table V. The run was carried out with a de-propanized ethylene feed containing 821 ppm CO.
$^g$ See Table VI

The results in Table VII indicate that the invention catalysts using a spinel as support are as good as, or better than, the catalysts using an alumina as support.

EXAMPLE VII

This example illustrates the measurement of skin thickness of palladium, or the depth of palladium deposition on a support surface.

The runs were carried out as follows: For each sample, representative pellets were embedded in epoxy (obtained from Buehler, Ltd., Lake Bluff, Illinois) and allowed to polymerize overnight. A thin cut was made with a Buehler Isomet diamond saw to expose the interior of the embedded pellets. This exposed surface was polished...
through successively smaller grit polishing media, finishing with submicron colloidal silica. Each polished sample was coated with a thin layer of carbon in a vacuum evaporator to provide conductivity for examination in the electron microprobe.

The instrument used for the analyses was a JEOL 733 electron microprobe with Noran Voyager stage and spectrometer automation. Instrument parameters include 20 kilovolts accelerating voltage, 40 nanoamp beam current, and a focused electron beam. Line traverses to determine the metal deposition in the pellet interior were set up to start at the outer rim and to end at or near the center. Intervals between the analysis points were varied to define the deposition profile. Within the outer 200 micrometers of the traverse, the interval ranged from 2 to 10 micrometers. From there to the pellet center, the interval was approximately 120 micrometers. For examples that did not have silver addition, traverses to the pellet center were done on only one pellet and only the outer 200 micrometers were analyzed on the remaining pellets in order to save analysis time.

To determine the maximum depth of effective palladium deposition, the concentration at each analysis point was normalized to the maximum concentration in that traverse. For comparison purposes, the penetration depth for palladium was considered to be the point where the deposition dropped to a normalized value of 0.1 compared to 1.0 for the maximum concentration. This distance was typically at the point where the rapid decrease in the palladium deposition ended and was always before the concentration dropped below the detection limit of the analysis technique (0.02 weight %). To get finer detail from the data, the distance that corresponded to the normalized value of 0.1 was interpolated from adjacent analysis points.

The results in Table VIII below indicate that palladium deposition on the alumina support was deeper into the pellet (69 micrometers) compared to 24 micrometers within zinc aluminate, and 33 within magnesium aluminate. The average depth of palladium deposition on zinc aluminate support was, in fact, statistically the same as the magnesium aluminate support.
TABLE VIII

<table>
<thead>
<tr>
<th>Catalyst Support</th>
<th>Alumina</th>
<th>Zinc Aluminate</th>
<th>Magnesium Aluminate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skin thickness (µm)</td>
<td>69&lt;sup&gt;a&lt;/sup&gt;</td>
<td>24&lt;sup&gt;b&lt;/sup&gt;</td>
<td>33 (35)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>The value was average of measurements of 6 catalyst pellets. The catalyst is disclosed in Example III.

<sup>b</sup>The value was average of measurements of 6 catalyst pellets. The catalyst is disclosed in Example II.

<sup>c</sup>The value was average of measurements of 3 catalyst pellets. The value in the parenthesis was the result of a separate run and was average of measurements of 7 pellets in which silver was not present. The catalyst is disclosed in Example VI.

EXAMPLE VIII

This example illustrates the superior selectivity of a skin catalyst over a non-skin catalyst.

The skin catalyst used was the same as that disclosed in Example VI. The non-skin catalyst was prepared as follows. First, a PdCl<sub>2</sub> solution was made by weighing 0.159 g PdCl<sub>2</sub> into a 10 ml beaker followed by adding 1.0 g conc. HCl to the beaker. Upon heating for 30 minutes, not to dryness, the PdCl<sub>2</sub>/HCl liquid was transferred to a bottle and diluted therein to 100 g with bottled water.

Secondly, 25.87 g of magnesium aluminate, prepared as described in Example VI was prepared. A portion (7.998 g) of the PdCl<sub>2</sub> solution prepared above in a 10 ml beaker was added 32 drops of conc. HCl (1.059 g) to prepare an acidified PdCl<sub>2</sub>. The magnesium aluminate was incipiently wetted with 7.187 g of the acidified PdCl<sub>2</sub> followed by drying at 85°C. for 2 hours, at 100°C. for 4 hours, and then 454°C. for 2 hours in 200 cc/min air to prepare Pd/MgAl<sub>2</sub>O<sub>4</sub>

Thirdly, an AgNO<sub>3</sub> solution, prepared by dissolving 0.100 g of AgNO<sub>3</sub> with 24.89 g of bottled water, was poured over the Pd/MgAl<sub>2</sub>O<sub>4</sub>. After 1 hour, with stirring every 15 minutes, excess AgNO<sub>3</sub> solution was poured off and the solid was blot-dried on paper towel, further dried at 85°C. for 15 hours, and calcined for 2 hours at 100°C. and then 2 hours at 454°C.

The skin catalyst and non-skin catalyst, both supported on MgAl<sub>2</sub>O<sub>4</sub>, were tested for selected hydrogenation as described in Example II. The results are summarized in Table IX below.
The results in Table IX shows that a skin catalyst had much lower cleanup temperature \( T_1 \) and higher selectivity \( \Delta F \) than a non-skin catalyst.

The results shown in the above examples also clearly demonstrate that the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those inherent therein. While modifications may be made by those skilled in the art, such modifications are encompassed within the spirit of the present invention as defined by the specification and the claims.

### TABLE IX*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd penetration (μm)</th>
<th>( T_1 (^\circ\text{F}) )</th>
<th>( T_2 (^\circ\text{F}) )</th>
<th>( \Delta F (^\circ\text{F}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skin</td>
<td>33 (35)(^b)</td>
<td>120</td>
<td>177</td>
<td>57</td>
</tr>
<tr>
<td>Non-skin</td>
<td>2500(^c)</td>
<td>221</td>
<td>259</td>
<td>38</td>
</tr>
</tbody>
</table>

*See footnote a, Table VII.

*Palladium was distributed throughout the catalyst pill having a radius of about 2500 μm.

The claims define:

1. A composition of hydrocarbon, said composition further comprises palladium and silver are each present at a concentration to effect hydrogenation of an unsaturated hydrocarbon.

2. A composition wherein the skin catalyst is skin distributed on the surface of the composition.

3. A composition wherein the skin catalyst is in the range of from about 5 to about 15.

4. A composition wherein palladium is in the range of from 10 to about 20.

5. A composition wherein palladium is further comprises an alkali metal.

6. A composition wherein said compound is an alkali metal fluorosalvinate.

7. A composition wherein metal of said spinel is zinc, manganese, zirconium, iron, or a combination of any two or more.

8. A composition wherein the aluminate, magnesium aluminate, or magnesium thereof.

9. A composition wherein weight % of said palladium is in the range of 5 to about 15.

10. A composition wherein weight % of said palladium is in the range of from about 10 to about 20.

11. A composition wherein weight % of said silver is in the range of from about 5 to about 15.

12. A composition wherein weight ratio of silver to palladium is in the range of from about 0.05 to about 0.25.

13. A composition wherein weight ratio of silver to palladium is in the range of from 0.1 to about 0.2.

14. A composition wherein...
The claims defining the invention are as follows:

1. A composition useful as a catalyst for hydrogenating an unsaturated hydrocarbon, said composition comprising palladium, silver, and a spinel, wherein said palladium and silver are each present in a sufficient amount to effect said hydrogenation of an unsaturated hydrocarbon.

2. A composition according to claim 1, wherein said palladium is present as skin distributed on the surface of said spinel.

3. A composition according to claim 2, wherein the thickness of said skin is in the range of from about 5 to about 500 \( \mu \text{m} \).

4. A composition according to claim 3, wherein the thickness of said skin is in the range of from 10 to about 100 \( \mu \text{m} \).

5. A composition according to any one of the preceding claims, which further comprises an alkali metal-containing compound.

6. A composition according to claim 5, wherein said alkali metal-containing compound is an alkali metal fluoride.

7. A composition according to any one of the preceding claims, wherein the metal of said spinel is zinc, magnesium, calcium, beryllium, strontium, barium, radium, iron, manganese, zirconium, molybdenum, ruthenium, rhodium, cobalt, germanium, tin or a combination of any two or more thereof.

8. A composition according to claim 7, wherein said spinel is zinc aluminate, magnesium aluminate, zinc titanate, or a combination of any two or more thereof.

9. A composition according to any one of the preceding claims, wherein the weight % of said palladium is in the range of from about 0.0001 to about 3%.

10. A composition according to claim 8, wherein the weight % of said palladium is in the range of from about 0.0005 to 1.5%.

11. A composition according to claim 10, wherein the weight % of said palladium is in the range of from about 0.001 to 1.5%.

12. A composition according to any one of the preceding claims, wherein the weight % of said silver is in the range of from about 0.001 to about 3%.

13. A composition according to any one of the preceding claims, wherein the weight ratio of silver to palladium is in the range of from about 0.1:1 to about 20:1.

14. A composition according to claim 13, wherein the weight % of said
palladium is in the range of from about 0.001 to about 1.0%; and the weight ratio of silver to palladium is in the range of from about 3:1 to about 8:1.

15. A hydrogenation process comprising contacting a highly unsaturated hydrocarbon, in the presence of hydrogen, with a composition according to any one of the preceding claims, under a condition sufficient to effect selective hydrogenation of said highly unsaturated hydrocarbon to a less unsaturated hydrocarbon.

16. A process according to claim 15, wherein said hydrogen is present in said highly unsaturated hydrocarbon.

17. A process according to claim 15, wherein said hydrogen is fed separately and mixed with said highly unsaturated hydrocarbon prior to said contacting with said composition.

18. A process according to any one of claims 15-17, wherein said highly unsaturated hydrocarbon comprises a fluid which is water, steam, water containing a soluble or insoluble substance, or a combination of any two or more thereof.

19. A composition useful as a catalyst for hydrogenating an unsaturated hydrocarbon said composition substantially as herein described with reference to any one of the Examples.

20. A hydrogenation process substantially as herein described with reference to any one of the Examples.

DATE: 25th August, 1997
PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
PHILLIPS PETROLEUM COMPANY
ABSTRACT OF THE DISCLOSURE

A composition and a process for using the composition in a selective hydrogenation of a highly unsaturated hydrocarbon such as, for example, an alkyne or diolefin, to a less unsaturated hydrocarbon such as, for example, an alkene or a monoolefin, are disclosed. The composition comprising palladium, silver, and a spinel wherein the palladium and silver are each present in a sufficient amount to effect the selective hydrogenation of an unsaturated hydrocarbon. Optionally, the palladium is present as skin distributed on the surface of the spinel. The composition can further comprise an alkali metal-containing compound such as, for example, potassium fluoride.