

Catalyst Composition Usefull For Hydrogenation Of Dienes

In one aspect, this invention relates to a supported noble metal catalyst composition. In another aspect, this invention relates to a selective diolefin (diene) hydrogenation process employing a supported noble metal catalyst composition. In still a further aspect, this invention relates to a process for the selective hydrogenation of 1,3-butadiene to butenes employing a supported noble metal catalyst composition.

Catalysts comprising palladium, silver and a support material are known diene hydrogenation catalysts. For instance, U.S. Patent 4,409,410 discloses the use of a Pd/Ag/Al₂O₃ catalyst for the selective hydrogenation of butadiene to butenes. Even though supported Pd/Ag catalysts are effective hydrogenation catalysts, there is an ever present need for further improvements (e.g., for enhanced selectivity to monoolefins and/or increased catalyst life). The present invention is directed to an improved, modified catalyst compositions and its use in processes for the selective hydrogenation of diolefins to monoolefins, preferably of 1,3-butadiene to butenes. The present invention provides an improved palladium/silver-containing catalyst composition which may be used in the selective hydrogenation of diolefins to monoolefins, such as in the selective hydrogenation of 1,3-butadiene to butenes.

In accordance with this invention, a catalyst

CASE: 33287

composition is provided which comprises (a) at least one palladium-containing material selected from the group consisting of palladium metal and palladium compounds, (b) at least one silver-containing material selected from the group consisting of silver metal and silver compounds, (c) at least one alkali metal fluoride, and (d) at least one inorganic support material. In a preferred embodiment, the inorganic support is alumina and the alkali metal fluoride is potassium fluoride.

Also in accordance with this invention, an improved process for selectively hydrogenating C_4 - C_{10} diolefins with hydrogen gas to the corresponding C_4 - C_{10} monoolefins is carried out with the catalyst composition of this invention. In a preferred embodiment, 1,3-butadiene (more preferably present in small amounts in butene-containing gas streams) is selectively hydrogenated with hydrogen gas to at least one butene in the presence of the catalyst composition of this invention.

The inventive composition comprises (preferably consists essentially of) (a) palladium metal and/or at least one palladium compound (preferably palladium oxide), (b) silver metal and/or at least one silver compound (preferably silver oxide), (c) at least one alkali metal fluoride (preferably potassium fluoride), and (d) an inorganic support material selected from the group consisting of alumina, silica, titania, zirconia, aluminosilicates, zinc aluminate, zinc titanate, and mixtures of two or more than two of these compounds, preferably alumina, more preferably alpha-alumina. Generally, the catalyst composition comprises 0.01-2 (preferably about 0.05-0.6) weight-% Pd, about 0.02-10 (preferably about 0.1-5) weight-% Ag, and about 0.05-10 weight-% (preferably about 0.2-5) weight-% alkali metal (preferably K). By use of the term "consists essentially of", it is

intended that the catalyst composition does not include any component which would materially affect the desired properties imparted to the catalyst by the components recited after this term.

- 5 The catalyst particles can have any suitable shape (spherical, cylindrical, trilobal and the like), and are preferably either spheres or cylindrical extrudates. The catalyst particles can have any suitable particle size, and generally have a size of
- 10 about 1-10 mm (preferably about 2-6 mm). The catalyst particles can have any suitable surface area (measured by the BET method by Bruhauer, Emmett and Teller employing N_2), and generally have a surface area of about 1-200 (preferably about 10-100) m^2/g .
- 15 The catalyst particles can be prepared by any suitable means. The promoter components (a), (b) and (c) can be deposited onto and/or incorporated into the inorganic support material by any suitable means and in any suitable order. For instance, the alkali metal
- 20 fluoride can be incorporated into the support material, followed by impregnation of the fluoride-containing support material with Pd and Ag compounds (such as H_2PdCl_4 and $AgNO_3$), sequentially in any order or simultaneously, followed by drying and calcining of the
- 25 thus-impregnated composition. Or a supported palladium catalyst composition (preferably a Pd/Al_2O_3 composition which is commercially available, e.g., from Mallinckrodt Specialty Chemicals Company, Erie, PA) can be impregnated with a silver compound and an alkali
- 30 metal fluoride, either sequentially in any order or simultaneously, followed by drying and calcining of the thus-impregnated composition. Mainly for economic reasons, it is presently not preferred to prepare the catalyst composition by a method which includes an
- 35 additional low-temperature wet-reduction step (i.e., treatment with a reducing agent dissolved or dispersed in a liquid medium, at a temperature of up to about

60°C.). Preferably, the catalyst composition of this invention is prepared by incorporating alkali metal fluoride into a supported Pd/Ag-containing base catalyst, as-described below.

5 The preferred starting material (also referred to as "base catalyst") which is to be improved in accordance with this invention by incorporation of alkali metal fluoride therein, can be any supported palladium- and silver-containing composition. The base
10 catalyst composition can be a fresh butadiene hydrogenation catalyst; or it can be a used and thereafter oxidatively regenerated butadiene hydrogenation catalyst composition; or it can be a butadiene hydrogenation catalyst composition which has
15 previously been treated with a wet-reducing agent (such as dissolved formaldehyde, formic acid, ascorbic acid, dextrose, hydrazine, alkali metal borohydride and the like), at a low temperature of up to about 60°C. (preferably about 10-50°C.), as has been described in
20 Example I. Broadly, the base catalyst can contain about 0.01-2 (preferably about 0.05-0.6) weight-% Pd, about 0.02-10 (preferably about 0.1-5) weight-% Ag and a suitable solid inorganic support material, preferably alumina (more preferably alpha-alumina). Preferably,
25 the Ag:Pd weight ratio in the catalyst is about 1:1 to about 20:1, more preferably about 2:1 to about 10:1. The supported Pd/Ag base catalyst particles can have any suitable shape, and preferably are spherical pellets or cylindrical extrudates. The size of these
30 supported Pd/Ag base catalyst particles generally is about 1-10 mm, preferably about 2-6 mm, and its surface generally is about 1-200 m²/g.

 In the preferred method of preparing the catalyst composition of this invention, a Pd/Ag-
35 containing base catalyst (described above) is contacted with a solution (preferably aqueous) of at least one alkali metal fluoride (preferably KF) at such

conditions as to incorporate about 0.05-10 (preferably about 0.2-5) weight-% of alkali metal (preferably potassium) into the catalyst composition. Generally, the concentration of the alkali metal fluoride in the contacting (impregnating) solution is about 0.1-10 mol/l (preferably about 0.2-3 mol/l). The preferred contacting method is "incipient wetness impregnation", i.e. essentially completely filling the pores of the base catalyst with the alkali metal fluoride solution. Generally, the weight ratio of the solution to the solid base catalyst composition is in the range of about 0.2:1 to about 2:1, preferably about 0.4:1 to about 1:1 (depending on the fluoride concentration of the impregnating solution and the desired alkali metal fluoride level in the catalyst composition of this invention). Thereafter, the catalyst composition is substantially dried (preferably at about 50-150°C. for about 0.5-20 hours) and calcined (preferably in an oxidizing gas atmosphere, more preferably air) at a temperature of about 300-600°C. (preferably about 300-500°C.) for about 0.2-20 hours (preferably about 1-8 hours).

The catalyst composition of this invention is preferably employed in the selective hydrogenation of diolefins containing 4-10 carbon atoms per molecule to the corresponding monoolefins containing 4-10 carbon atoms per molecule, particularly of 1,3-butadiene to primarily butenes (butene-1, butene-2). The calcined catalyst composition of this invention can be employed directly in this selective hydrogenation process. However, it is preferred to first treat the catalyst with a reducing gas such as hydrogen, because the optimum operation of the selective hydrogenation does not begin until there has been a substantial reduction of the catalytic metals. Typically, the reduction is carried out at a temperature in the range of about 10°C. to about 100°C. for at least 10 minutes

(preferably about 1-10 hours).

Non-limiting examples of suitable diolefins containing 4-10 carbon atoms per molecule which can be hydrogenated in the process of this invention include

5 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1, 2-pentadiene, 2,3-dimethyl-1, 3-butadiene, heptadienes, octadienes, nonadienes, decadienes, cyclopentadiene,

10 cyclohexadiene, methylcyclopentadienes, cycloheptadienes, methylcyclohexadienes, dimethylcyclopentadienes, ethylcyclopentadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes,

15 methyloctadienes, dimethylheptadienes, ethylheptadienes, trimethylheptadienes, and mixtures of one or two of these diolefins. Presently preferred are diolefins containing 4-6 carbon atoms per molecule.

The diolefin-containing feed for the

20 hydrogenation process of this invention can also contain other hydrocarbons, in particular, monoolefins. Non-limiting examples of such monoolefins which can be present in the feed at a level of at least 30 volume-% include ethylene, propylene, 1-butene, 2-butene,

25 isobutylene, 1-pentene, 2-pentene, methyl-1-butenes (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes,

30 methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentenenes, cycloheptene,

35 methylcyclohexenes, dimethylcyclopentenenes, ethylcyclopentenenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes,

trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and mixtures of two or more than two of these monoolefins.

Presently preferred are monoolefins containing 4-6
5 carbon atoms per molecule.

The fluid feed (which may be liquid or gaseous at the hydrogenating conditions of this process) generally contains about 0.01-70 mole-% of at least one diolefin, preferably about 0.01 to about 10
10 mole-% of at least one diolefin. Generally, the fluid feed comprises at least one diolefin and additionally at least one monoolefin, preferably about 30-99.9 mole-% of at least one monoolefin. However, it is within the scope of this invention to employ feeds which
15 contain more than about 70 mole-% of at least one diolefin, or even to employ feeds which consist essentially of at least one diolefin. Also, the feed can contain small amounts (generally less than about 0.01 mole-%) of sulfur compounds (such as H_2S ,
20 mercaptans, organic sulfides) and/or carbon monoxide (also generally less than about 0.01 mole-%) as impurities.

The selective hydrogenation process of this invention is generally carried out by contacting a feed
25 stream containing at least one diolefin and molecular hydrogen with the catalyst (generally contained in a fixed bed). Generally, about 1-10 moles of hydrogen are employed for each mole of diolefin. The temperature necessary for the selective hydrogenation
30 process of this invention depends largely upon the activity of the catalyst and the desired extent of diolefin hydrogenation. Generally, temperatures in the range of about 35°C. to about 200°C. are used. A suitable reaction pressure generally is in the range of
35 about 20 to 2,000 pounds per square inch gauge (psig). The liquid hourly space velocity (LHSV) of the hydrocarbon feed can vary over a wide range.

Typically, the space velocity of the feed will be in the range of about 3 to about 100 liters of hydrocarbon feed per liter of catalyst per hour, more preferably about 20 to about 80 liter/liter/hour. The

5 hydrogenation process conditions should be such as to avoid significant hydrogenation of monoolefins (formed by hydrogenation of diolefins and/or being initially present in the feed) to paraffins.

10 In the preferred embodiment of the selective hydrogenation process of this invention, a hydrocarbon feed stream containing 1,3-butadiene and molecular hydrogen are contacted with the catalyst (generally contained in a fixed bed). Frequently, the hydrocarbon feed contains butenes as the primary components
15 (comprising in excess of about 50 weight-%) and 1,3-butadiene as a minor component (present at a level of about 0.01 to about 10 weight-% butadiene).

Preferably, this hydrogenation process employs about 1-2 moles H_2 per mole 1,3-butadiene. The reaction
20 temperature necessary for the selective hydrogenation of 1,3-butadiene depends largely upon the activity of the catalyst and the desired extent of the 1,3-butadiene hydrogenation, and generally is in the range of about 35°C. to about 100°C. Any suitable reaction
25 pressure can be employed. Generally, the total pressure is in the range of about 50 to 1,000 pounds per square inch gauge (psig). The liquid hourly space velocity (LHSV) of the hydrocarbon feed can also vary over a wide range. Typically, the space velocity will
30 be in the range of about 3 to about 100 liters of hydrocarbon feed per liter of catalyst per hour, more preferably about 20 to about 80 liter/liter/hour. The hydrogenation process conditions should be such as to avoid significant hydrogenation of butenes to butane.

35 Regeneration of the catalyst composition of this invention (after it has been employed in a diolefin hydrogenation process) can be accomplished by

heating the catalyst in an oxidizing gas, preferably air, at a temperature preferably not in excess of 700°C. (preferably at a temperature about 500-650°C.) for a time period in the range of about 10 minutes to about 20 hours, to burn off any deposited or adsorbed organic matter (e.g., polymeric substances) or char. The regenerated catalyst can be reemployed in the selective hydrogenation process of this invention, generally after reduction with hydrogen, as described above.

The following examples are presented to further illustrate this invention and should not be construed as unduly limiting the scope of this invention.

Example I

This example illustrates the preparation of various palladium-containing catalysts and their use in the selective hydrogenation of 1,3-butadiene to butenes.

Catalyst A1 (Control) was a Pd/Ag/Al₂O₃ catalyst, which had been provided by the Calsicat Catalyst Division of Mallinckrodt Specialty Chemicals Company, Erie, PA. This catalyst had a BET/N₂ surface area of 35 m²/g, a bulk density of 0.90 cc/g, and a particle size of 8-14 mesh. It contained 0.28 weight-% Pd and 1.85 weight-% Ag.

Catalyst A2 (Control) was prepared in a R&D laboratory of Phillips Petroleum Company, Bartlesville OK by the following procedure: 20.03 grams of a Pd/Al₂O₃ catalyst (1/16 inch spheres containing about 0.3 weight-% Pd, marketed by Calsicat under the product designation of "E-143 SDU") were soaked for about 1 hour in 22 cc of an aqueous solution containing 1.03 gram of AgNO₃. Thereafter, excess solution was drained off, the soaked catalyst was dried at 190°F. for several hours, and the dried catalyst was calcined in air at 370°C. for 5 hours. This catalyst contained

0.35 weight-% Pd and 3.0 weight-% Ag.

Catalyst B (Invention) was prepared by soaking 80.17 grams of Calsicat E-143SDU (described above) with an aqueous solution of 4.08 grams of AgNO_3 in 72.3 grams of H_2O for about 1.5 hours. Excess liquid was drained from the Ag-impregnated catalyst, which was then dried at 180°F . for several days and calcined for 4.5 hours at 370°C . in air. Then 20.07 g of this Pd/Ag/ Al_2O_3 catalyst material was soaked in 30 cc of a formaldehyde solution containing about 37 weight-% of formaldehyde, about 17 weight-% of methanol, and about 46 weight-% of water. About 0.5 g solid KOH was added to this mixture of catalyst and formaldehyde solution which was then stirred for 45 minutes. Thereafter, another aliquot of about 0.5 g solid KOH was added to this mixture. After soaking for 20 minutes, excess liquid was drained off, the catalyst was washed twice with methanol and then twice with distilled water (until the filtrate had a pH of about 7). This wet-reduced, catalyst, from which KOH had been removed by the above washing procedure, was dried overnight at 180°F . The dried catalyst was then impregnated with a solution of 0.441 g KF in 14.15 g H_2O . A large portion of water was removed from the mixture by heating at 180°F . (without prior draining of excess liquid). The obtained KF-impregnated Pd/Ag/ Al_2O_3 catalyst was then dried overnight at 132°C . and calcined in air at 370°C . for 3 hours. Catalyst B contained about 0.28 weight-% Pd, about 2.6 weight-% Ag and about 1.3 weight-% K.

The above-described catalyst materials were tested in the selective hydrogenation of 1,3-butadiene by the following procedure. About 20 cc of each catalyst was placed into a stainless steel reactor tube having an inner diameter of 0.5 inch and a length of about 18 inches. Thermocouples were inserted into the top and bottom regions of the catalyst bed, which was

heated by an external furnace. The hydrocarbon feed was liquid and contained about 5.1 mole-% 1,3-butadiene, about 16.4 mole-% cis-butene-2, about 27.4 mole-% trans-butene-2, about 44.1 mole-% butene-1, about 6.8 mole-% n-butane, and about 0.1 weight-% C₆+ hydrocarbons. Hydrogen gas was fed with the liquid hydrocarbon feed so as to provide a H₂/butadiene mole ratio of about 1:1. The total pressure in the reactor was maintained at about 500 psig. The product gas was analyzed every 1-3 hours by means of a gas chromatograph. Pertinent process parameters and test results are summarized in Table I.

Table I

Catalyst	Feed Rate of Liquid Hydrocarbons (cc/minute)	Feed Rate of Hydrogen Gas (cc/minute)	Average Reaction Temp. (°F.)	% Conversion of Butadiene	% Selectivity to Butenes	% Selectivity to Butane
Al (Control)	9	104	106	73.7	64.1	35.8
	9	104	104	76.2	67.9	32.2
	9	104	104	78.4	70.9	29.1
	9	104	107	77.6	71.2	29
	9	104	108	78.6	74.6	25.4
	9	104	106	78.5	74.4	25.8
	9	104	108	78.9	75.8	24.3
	18	217	111	84.7	82.7	17.2
	18	217	108	83.9	84.9	15.5
	18	217	107	84.7	85.6	14.7

Table I (continued)

Catalyst	Feed Rate of Liquid Hydrocarbons (cc/minute)	Feed Rate of Hydrogen Gas (cc/minute)	Average Reaction Temp. (°F.)	% Conversion of Butadiene	% Selectivity to Butenes	% Selectivity to Butane
	18	217	106	84.7	84.9	15.4
	18	217	108	84.1	86	14.4
A2 (Control)	18	218	84	73.1	72.2	27.3
	18	218	97	85.1	83.7	15.4
	18	218	97	84.6	83.9	15.2
	18	218	104	84.8	83.4	15.7
	18	218	122	76.0	54.6	46.0
	18	218	123	75.4	60.8	39.8
	18	218	138	74.5	60.1	40.5
	18	218	141	74.0	70.4	30.1

Table I (continued)

Catalyst	Feed Rate of Liquid Hydrocarbons (cc/minute)	Feed Rate of Hydrogen Gas (cc/minute)	Average Reaction Temp. (°F.)	% Conversion of Butadiene	% Selectivity to Butenes	% Selectivity to Butane
B (Invention)	9	104	130	89.0	90.4	9.7
	9	104	122	90.4	91.7	8.4
	9	104	119	89.8	92.4	7.7
	9	104	117	88.6	92.5	7.5
	9	104	118	89.9	91.6	8.6
	9	104	100	88.6	93.5	6.6
	9	104	98	87.0	94.0	6.0
	9	104	99	87.1	94.0	6.1
	9	104	98	87.0	94.3	5.7
	9	104	107	88.9	92.1	7.8
	9	104	106	86.8	92.7	7.4
	9	104	89	85.2	93.7	6.5

Table I (continued)

Catalyst	Feed Rate of Liquid Hydrocarbons (cc/minute)	Feed Rate of Hydrogen Gas (cc/minute)	Average Reaction Temp. (°F.)	% Conversion of Butadiene	% Selectivity to Butenes	% Selectivity to Butane
	9	104	90	83.6	94.2	5.8
	9	104	88	82.4	94.1	5.7
	9	104	94	88.1	95.1	5.1
	9	104	90	85.2	95.0	5.1
	9	104	88	84.0	95.5	4.6
	9	104	91	84.5	95.4	4.7
	9	104	98	84.4	95.4	4.6
	9	104	100	85.2	95.0	5.1
	9	104	100	85.4	95.1	5.0

Test data in Table I clearly show that the promotion of a Pd/Ag/Al₂O₃ catalyst with KF (resulting in Catalyst B) had a consistent beneficial effect on attained 1,3-butadiene conversion and selectivity to butenes (combined yields of butene-1 and butene-2 divided by butadiene conversion) versus control catalysts A1 and A2 (Pd/Ag/Al₂O₃ which had not been treated with KF). These test data also show that during the invention test, which lasted about 24 hours, Catalyst B exhibited good catalytic stability, as evidenced by a rather small drop in butadiene conversion and actually a slight increase in selectivity to the desired butenes. Thus, the butene yield (conversion times selectivity to butenes) remained approximately constant. Additional test data (not described herein) showed that the promotion of control catalyst A1 (Pd/Ag/Al₂O₃) with another potassium compound, KOH, resulted in a catalyst which exhibited unsatisfactory stability in a lengthy butadiene hydrogenation test, as evidenced by a significant decrease in catalytic activity and by process control (especially temperature control) problems.

Example II

This example further illustrates the use of another KF-treated Pd/Ag/Al₂O₃ composition as a catalyst in the selective hydrogenation of 1,3-butadiene.

Catalyst C (Invention) was prepared by soaking 20.15 g Catalyst A1 (Pd/Ag/Al₂O₃, disclosed in Example I) with an aqueous solution of 1.448 g of KF in 14.3 g of distilled water. The obtained material was dried at 180°F. for several hours and calcined at 235°C. for 1.5 hour.

Catalyst C was tested as a catalyst in the selective hydrogenation of 1,3-butadiene to butenes, substantially in accordance with the procedure

described in Example I, except that the liquid hydrocarbon feed contained 36.4 mole-% 1,3-butadiene, 13.1 mole-% trans-butene-2, 13.2 mole-% cis-butene-2, 30.2 mole-% butene-1, 7.2 mole-% n-butane, and 0.01 mole-% C₆+ hydrocarbons. The total reactor pressure was about 500 psig. The feed rate of the liquid hydrocarbon feed ranged from about 1.5 cc/minute (during the first two days) to about 3.0 cc/minute (during the last day), and the feed rate of H₂ gas ranged from about 140 cc/minute (during the first day) to about 320 cc/minute (during the last day). A portion of the product was recycled to the reactor so as to attain a 3-6:1 recycle:feed volume ratio. The reaction temperature in the center of the catalyst bed was about 90-100°F. during the entire test which lasted about 5 days. When the reaction had reached a steady state (after about 12 hours), the 1,3-butadiene content in the product ranged from about 6.0 mole-% to about 4.5 mole-% (during the last day), and the n-butane content in the product ranged from about 8.8 to about 8.2 mole-%. Thus, Catalyst C exhibited good catalytic activity and selectivity (to butenes). Furthermore, the fact that the catalyst performance did not deteriorate toward the end of the test (but actually improved in terms of feed conversion) indicates good stability of Catalyst C.



1. A catalyst composition useful for hydrogenation of dienes which comprises (a) at least one palladium-containing material which is palladium metal or a palladium compound, (b) at least one silver-containing material which is silver metal or a silver compound, (c) at least one alkali metal fluoride, and (d) at least one inorganic support material.
2. A composition according to claim 1, wherein said at least one inorganic support material is alumina, silica, titania, zirconia, an aluminosilicate, zinc aluminate, zinc titanate, or a mixture of any two or more of said inorganic support materials.
3. A composition according to claim 2, wherein said at least one inorganic support material is alumina.
4. A composition according to any one of claims 1-3, wherein said alkali metal is potassium.
5. A composition according to any one of the preceding claims, which comprises about 0.01-2 weight-% palladium, about 0.02-10 weight-% silver, and about 0.05-10 weight-% of alkali metal.
6. A composition according to claim 5, which comprises about 0.05-0.6 weight-% palladium, about 0.1-5 weight-% silver, and about 0.2-5 weight-% alkali metal.
7. A composition according to any one of the preceding claims, wherein the weight-ratio of silver to palladium is about 2:1 to about 10:1.
8. A composition according to any one of the preceding claims, wherein said composition has a particle size of about 1-10 μ m and a surface area of about 1-200 m^2/g .
9. A composition according to any one of the preceding claims, which is prepared by (i) impregnating a solid material which comprises components (a), (b) and (d) with a solution which comprises at least one alkali metal fluoride under impregnating conditions such that about 0.05-10 of said at least one alkali metal fluoride is incorporated into said material, (ii) drying the thus-impregnated, solid material,



and (iii) calcining the dried solid material at a temperature of about 300-600°C.

10. A composition according to claim 9, wherein said solid material comprising components (a), (b) and (d) contains about 0.01-2 weight-% Pd and about 0.02-10 weight-% Ag, and has a surface area of about 1-200 m²/g.

11. A process for selectively hydrogenating a diolefin containing 4-10 carbon atoms per molecule with hydrogen gas to a monoolefin containing 4-10 carbon atoms per molecule, which comprises contacting a hydrocarbon feed comprising at least one diolefin under suitable reaction conditions with a catalyst composition according to any one of the preceding claims to produce at least one monoolefin.

12. A process according to claim 11, wherein said at least one diolefin contains 4-6 carbon atoms per molecule, and said at least one monoolefin contains 4-6 carbon atoms per molecule.

13. A process according to claim 11 or 12, wherein the diolefin is present in a feed at a level of about 0.01-70 mole-%.

14. A process according to any one of claims 11-13, wherein said feed is a fluid feed which further comprises at least one monoolefin.

15. A process according to claim 14, wherein said monoolefin in said fluid feed contains 4-6 carbon atoms per molecule.

16. A process according to claim 15, wherein said monoolefin is a butene.

17. A process according to any one of claims 14-16, wherein said feed contains primarily said monoolefin and about 0.01-10 weight-% of said diolefin.

18. A process according to any one of claims 11-17, wherein said at least one diolefin is 1,3-butadiene.

19. A process according to claim 18, wherein about 1-2 moles of hydrogen are employed for each mole of 1,3-butadiene present in said feed.

20. A process according to any one of claims 11-19, wherein said suitable reaction conditions include a



- 20 -

temperature in the range of about 35-100°C., and a pressure in the range of about 50-1000 psig.

21. A process according to any one of claims 11-20, wherein said feed has a liquid hourly space velocity of about 3-100 liters per liter catalyst composition per hour.

A B S T R A C T

Catalyst Composition Usefull For Hydrogenation Of Dienes

A supported catalyst composition, which is effective as a diolefin hydrogenation catalyst, comprises palladium, silver and alkali metal fluoride. This catalyst composition is employed in the selective hydrogenation of C_4 - C_{10} diolefins (preferably 1,3-butadiene) with hydrogen gas to the corresponding monoolefins.