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[54] METHOD OF PREVENTING DOUBLE
BOND MIGRATION OF MONO-
OLEFINIC HYDROCARBONS IN
SELECTIVE HYDROGENATION

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[57]

ABSTRACT

A method of preventing double bond migration of a mono-olefin hydrocarbon during the selective hydrogenation of a polyunsaturated hydrocarbon coexisting with a mono-olefinic hydrocarbon, each of the mono-olefinic hydrocarbons and polyunsaturated hydrocarbons having at least four carbon atoms, in the presence of hydrogen, using a palladium- or nickel-hydrogenation catalyst, which comprises adding carbon monoxide to the reaction system in an amount of from 1 to 50 mol. % based on said hydrogen during the initial stage of the selective hydrogenation reaction and following the initial stage, lowering the content of carbon monoxide to a range of from 0.05–1 mol. % based on the hydrogen.

18 Claims, No Drawings

METHOD OF PREVENTING DOUBLE BOND MIGRATION OF MONO-OLEFINIC HYDROCARBONS IN SELECTIVE HYDROGENATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of preventing the double bond migration of mono-olefinic hydrocarbons during the selective hydrogenation of polyunsaturated hydrocarbons of polyolefinic and/or acetylenic types coexisting with said mono-olefinic hydrocarbons, each of the mono-olefinic hydrocarbons and the polyunsaturated hydrocarbons having at least four carbon atoms.

2. Description of the Prior Art

It is generally known that a polyunsaturated hydrocarbon of the polyolefinic and/or acetylenic type having at least four carbon atoms, coexisting with a mono-olefinic hydrocarbon having at least four carbon atoms, may be hydrogenated in the presence of a hydrogenation catalyst, such as palladium, platinum or nickel, by hydrogen to selectively convert said polyunsaturated hydrocarbons into the corresponding mono-olefinic hydrocarbons. Such a process is hereinafter referred to as "selective hydrogenation." For example, it is widely known that a butene fraction containing C_4 -diolefins and/or C_4 -acetylenes may be selectively hydrogenated in the presence of a palladium, platinum or nickel catalyst by hydrogen to convert said C_4 -diolefins and/or C_4 -acetylenes into the corresponding butenes, with little loss of butenes, thereby obtaining the butene fraction substantially free from said C_4 -diolefins and C_4 -acetylenes.

However, the conventional hydrogenation catalysts, such as palladium, platinum and nickel, used for such selective hydrogenation processes possess the disadvantage of promoting double bond migration in addition to the desired hydrogenation of the unsaturated bonds. Accordingly, conventionally practiced selective hydrogenation employing such catalysts are inevitably accompanied by double bond migration of mono-olefinic hydrocarbons.

For example, in the selective hydrogenation of the butene fraction containing 1-butene, C_4 -diolefins (e.g., 1,3-butadiene, methyl allene) and/or C_4 -acetylenes e.g., dimethyl acetylene, ethyl acetylene, vinyl acetylene) in the conventional process, both the selective hydrogenation reaction of C_4 -diolefins and/or C_4 -acetylenes into butenes and the double bond migration of 1-butene into 2-butene take place simultaneously under the same reaction condition. As a result, the greater part of the 1-butene is lost. This problem becomes very serious when it is desired to selectively hydrogenate C_4 -diolefins and/or C_4 -acetylenes coexisting with 1-butene to obtain a pure 1-butene or a fraction rich in 1-butene, free from C_4 -diolefins and C_4 -acetylenes. 1-butene and 1-butene-rich fractions are extremely useful as chemical feed materials for the production of poly-1-butene, 1-butene copolymer, etc.

Meanwhile, it has been known in the selective hydrogenation of ethylene containing acetylene in the presence of a hydrogenation catalyst to charge carbon monoxide or a sulfur compound (for example, hydrogen sulfide, mercaptans, carbon disulfide) into the reaction system; however, the carbon monoxide is not used to prevent the double bond migration of a mono-olefinic hydrocarbon, but is employed to increase the selectivity of the hydrogenation catalyst, i.e. for the purpose of facilitating the hydrogenation of acetylene selectively into ethylene without excessive hydrogenation of ethylene into ethane.

A process employing severe hydrogenation conditions, i.e. at a temperature of 93.3°–260° C. under pressure of 175–245 kg/cm²G, has been proposed in connection with preparing a mono-olefinic feedstock containing a minor proportion of polyolefin for oxoaldehyde synthesis. Under these severe conditions, skeletal isomerization of mono-olefinic hydrocarbons takes place in addition to the double bond migration.

There has also been described a process for the hydrogenation of acetylenes coexisting with di- and mono-olefins,

acetylenes and diolefins coexisting with mono-olefins over a copper catalyst containing a minute portion of an activating metal. However, when carbon monoxide is used to depress the hydrogenation of 1,3-butadiene, isomerization of 1-butene to 2-butene occurs.

Thus, it has been long desired in this art to develop a method of preventing the double bond migration of mono-olefinic hydrocarbons effectively during the selective hydrogenation of polyunsaturated hydrocarbons coexisting with mono-olefinic hydrocarbons.

We have described in our copending application, Ser. No. 828,186, how carbon monoxide (but not sulfur compounds) has the particular property of preventing double bond migration in selective hydrogenation of the aforesaid hydrocarbon mixtures, using known catalysts, and have claimed a method of preventing the double bond migration in which the hydrogenation is carried out in the presence of 1–50 mol. % of carbon monoxide, based on the hydrogen, through the entire reaction.

SUMMARY OF THE INVENTION

It is therefore the basic object of the present invention to provide a method for preventing the double bond migration of mono-olefinic hydrocarbons during the selective hydrogenation of polyunsaturated hydrocarbons coexisting with mono-olefinic hydrocarbons, each of the mono-olefinic hydrocarbons and polyunsaturated hydrocarbons having at least four carbon atoms, in the presence of hydrogen using a copper-free palladium or nickel hydrogenation catalyst.

Another object of the present invention is to provide a method of effectively preventing the double bond migration of mono-olefinic hydrocarbons during the selective hydrogenation of polyunsaturated hydrocarbons by the use of a small amount of carbon monoxide.

Still another object of the present invention is to provide a process for the selective hydrogenation of polyunsaturated hydrocarbons containing mono-olefinic hydrocarbons, each of said polyunsaturated hydrocarbons and mono-olefinic hydrocarbons having at least four carbon atoms, in the absence of the usual accompanying double bond migration.

Still another object of the present invention is to provide a method of inhibiting only the isomerization (double bond migration) activity of conventional hydrogenation catalysts being employed for the selective hydrogenation of polyunsaturated hydrocarbons coexisting with mono-olefinic hydrocarbons, each of said polyunsaturated hydrocarbons and mono-olefinic hydrocarbons having at least four carbon atoms.

These and other objects of the present invention will become more apparent from the following description thereof.

Accordingly, we have now found that double bond migration of mono-olefinic hydrocarbons can also be effectively prevented during the selective hydrogenation of polyunsaturated hydrocarbons coexisting with said mono-olefinic hydrocarbons, each of the mono-olefinic and polyunsaturated hydrocarbons having at least four carbon atoms, in the presence of hydrogen and a copper-free palladium or nickel hydrogenation catalyst, by carrying out said selective hydrogenation in the presence of 1–50 mol. %, preferably 5–30 mol. %, of carbon monoxide based on the hydrogen during the initial stage of the reaction and thereafter in the presence of 0.05–1 mol. % of carbon monoxide, based on the hydrogen.

DETAILED DESCRIPTION OF THE INVENTION

According to the process of this invention, the polyunsaturated hydrocarbons coexisting with the mono-olefinic hydrocarbons, each of which hydrocarbons having at least four carbon atoms, are selectively hydrogenated in the presence of hydrogen and 1–50 mol. % during the initial stage of the reaction and thereafter 0.05–1 mol. % of carbon monoxide, respectively based on the hydrogen, by the use of a

copper-free palladium or nickel catalyst. As a result, said polyunsaturated hydrocarbons are selectively hydrogenated and thus eliminated, and the double bond migration of said mono-olefinic hydrocarbons is effectively prevented. For instance, it is possible to effectively prevent the double bond migration, not only in the selective hydrogenation of 1,3-butadiene and/or other polyunsaturated hydrocarbons coexisting with butenes, but also in the selective hydrogenation of other C₃ or higher polyunsaturated hydrocarbons coexisting with higher mono-olefinic hydrocarbons, by the process of the present invention.

A hydrocarbon feed utilized in the selective hydrogenation of the present invention comprises a mixture of mono-olefinic hydrocarbon and a polyunsaturated hydrocarbon, each having at least four carbon atoms. Practically speaking, the hydrocarbon feed may contain hydrocarbons having up to 16 carbon atoms. The said polyunsaturated hydrocarbons are polyolefinic hydrocarbons (e.g., diolefins, triolefins and the like) and/or acetylenic hydrocarbons (e.g., alkynes, alkenynes). The content of the polyunsaturated hydrocarbons in the hydrocarbon feed is preferably less than about 50 mol. %. Feeds containing greater amounts of polyunsaturated hydrocarbons may, however, be employed within the scope of the invention. In addition, the hydrocarbon feed may contain paraffinic hydrocarbons, such as n-butane, pentane, hexane, etc.; inert gases such as hydrogen, nitrogen, etc.; and occasionally a small amount of C₃ polyunsaturated hydrocarbon, such as methyl acetylene and allene.

The hydrogen to be used in this invention may be either pure hydrogen or hydrogen-containing gases, such as natural gas, reformer off-gas, etc.

If the hydrocarbon feed already contains hydrogen, the rest of the hydrogen being required for the selective hydrogenation of this invention may be supplied from an external source. The amount of hydrogen employed in the present invention will vary depending upon the contents of the polyunsaturated hydrocarbon in the hydrocarbon feed. It is necessary to use more than the stoichiometric amount of hydrogen needed for hydrogenating the polyunsaturated hydrocarbons into corresponding mono-olefinic hydrocarbons. In general, 1-20,000 moles of hydrogen per total mole of polyunsaturated hydrocarbons may be employed for the selective hydrogenation.

The hydrogenation catalyst to be used in the present invention is a copper-free hydrogenation catalyst containing palladium or nickel. Suitable hydrogenation catalysts are palladium or nickel metals, or the sulfides or oxides of these metals, or such metals or compounds supported on known carriers, such as alumina, silica-alumina, magnesia, titania, diatomaceous earth, etc., by conventional treatment. Preferable catalysts are palladium supported on carrier (Pd cont. = 0.005-3 weight %) or nickel on a supported carrier (Ni cont. = 1-40 weight %).

To carry out the selective hydrogenation readily without the double bond migration of the mono-olefinic hydrocarbons, the hydrogen in the reaction system must contain 1-50 mol. %, preferably 5-30 mol. %, of carbon monoxide, based on the hydrogen present, during the initial stage of the reaction. In the initial stage of the reaction, an amount of carbon monoxide of less than 1 mol. % based on the hydrogen is not desirable, for double bond migration will take place along with the selective hydrogenation. When the content of carbon monoxide is also more than 50 mol. %, other disadvantages appear, such as prolongation of the reaction period for the selective hydrogenation of the polyunsaturated hydrocarbon. However, the double bond migration is still prevented.

The carbon monoxide may be introduced to the reaction system in any manner as long as hydrogen is also present. In practical operation, it is convenient to previously mix the carbon monoxide with hydrogen in a specific ratio and then to bring the resultant carbon monoxide-hydrogen mixture into contact with the hydrocarbon feed.

In accordance with the present invention, the content of carbon monoxide is thereafter (after the initial stage) lowered to a later (following the initial stage) range, i.e. 0.05-1 mol. % (based on the hydrogen present) at once, stepwise or continuously. Said later content of carbon monoxide in an amount of less than 0.05 mol. % is not desirable, since double bond migration will also take place along with the selective hydrogenation. If the later content of carbon monoxide is more than 1 mol. %, the double bond migration does not take place in the selective hydrogenation. However, said process wherein the amount of carbon monoxide is more than 1 mol. % is shown in our copending application as mentioned above. Naturally, it is no harm to the process of the present invention that the later content of carbon monoxide remains in the initial range, i.e. 1-50 mol. %. But economically, the smallest amount of carbon monoxide possible should be employed in the reaction since carbon monoxide is relatively expensive.

In the process of the present invention, the content of carbon monoxide is lowered from the initial range, i.e. 1-50 mol. % to the later range, i.e. 0.05-1 mol. % after the hydrogenation catalyst has been treated with a requisite amount of carbon monoxide under a high content (1-50 mol. %) of carbon monoxide during the initial stage of hydrogenation reaction. The content of carbon monoxide may usually be lowered to the later range of 0.05-1 mol. % after the total amount of carbon monoxide added to the reaction system comes to at least 0.05 moles per gram of the hydrogenation catalyst. The content of carbon monoxide can be lowered to the later range after the total amount of carbon monoxide comes to preferably at least 0.1-20 moles, most preferably at least 0.2-10 moles, per gram of the catalyst.

Industrially, new carbon monoxide is not added to the reaction system during the decrease of carbon monoxide content from the initial range (1-50 mol. %) to the later range (0.05-1 mol. %). On approaching of the carbon monoxide content to the later range, new carbon monoxide begins to be introduced into the reaction system along with hydrogen. In the restarting of the hydrogenation reaction following the interruption of the reaction, the content of carbon monoxide is enough in the later range (0.05-1 mol. %) provided that the catalyst is treated in the initial range with 1-50 mol. % of carbon monoxide at least once.

The selective hydrogenation of the present invention is preferably carried out at a temperature of 20°-250° C. under the pressure of about atmospheric to 50 kg/cm². Under such a relatively mild reaction condition, skeletal isomerization of the mono-olefinic hydrocarbons will not occur in any substantial amount during the selective hydrogenation. Whenever the content of carbon monoxide is lowered, it is preferable to employ the milder reaction conditions, e.g., to lower the temperature of hydrogenation reaction as shown in the examples. Said milder reaction conditions are chosen to prevent excessive hydrogenation. In this case, the double bond migration can be effectively prevented even though hydrogenation temperature is or is not lowered. The hydrocarbon feed is introduced as either an upflow or downflow to a reactor packed with the hydrogenation catalyst at a liquid hourly space velocity (L.H.S.V.) of 0.1-40 and is selectively hydrogenated therein. Although it is convenient to contact the hydrocarbon feed with the hydrogenation catalyst in a fixed bed, if necessary or desired a moving or fluidized bed may be employed. The selective hydrogenation may be carried out in either a batch, semicontinuous or continuous operation. It is also possible to introduce a sulfur compound, such as hydrogen sulfide, mercaptan or carbon disulfide together with carbon monoxide to the reaction system for the purpose of avoiding excessive hydrogenation in the process of this invention. However, the sulfur compound itself has no ability to prevent the double bond migration as mentioned above.

According to the process of this invention, it has now become possible to effectively prevent double bond migration in mono-olefinic hydrocarbons which has always accompanied conventional selective hydrogenation of mixtures of

mono-olefinic and polyunsaturated hydrocarbons having at least four carbon atoms. The process of this invention therefore has wide industrial applications not only as a process for selective hydrogenation in the absence of double bond migration but also as a process for the production of a particular hydrocarbon which may be altered during conventional selective hydrogenation by double bond migration.

The present invention is particularly useful in carrying out the selective hydrogenation of butenes containing C₄-diolefins and/or C₄-acetylenes without lowering the 1-butene content, and also in obtaining 1-butene, or a fraction rich in 1-butene, from 1-butene mixtures with C₄-diolefins and/or C₄-acetylenes by selective hydrogenation. However, the field of the application of the present invention is not limited only to these specific examples.

A better understanding of the present invention will be attained from the following examples, which are merely intended to be illustrative and not limitative of the present invention.

EXAMPLE 1

The hydrocarbon feed employed was a butene-containing feed having the composition shown in Table 1. Said butene feed is a raffinate extracted from a C₄ fraction produced by naphtha steam cracking.

The hydrogenation catalyst employed was a commercial palladium catalyst ("PGC-C" produced by Englehard Industries, Ltd.) containing 0.1 % by weight of palladium supported on alumina.

A vertically disposed reactor of 50 mm inner diameter was packed with 200 ml of the palladium catalyst. Into the reactor there were continuously introduced the butene feed at the rate of 600 ml/hr (L.H.S.V. = 3.0) and hydrogen containing 25 mol. % carbon monoxide at the rate of 60 liters (N.T.P.)/hr, at a temperature of 90° C. and pressure of 25 kg/cm², to effect the selective hydrogenation. The hydrogenated product thus obtained was analyzed by gas chromatography.

The composition of the hydrogenated product (except hydrogen and carbon monoxide) which is obtained after 2 hours from the start of selective hydrogenation, is given in the column headed "Product A" in Table 1.

After 4 days from the start of the reaction, the content of carbon monoxide, based on the amount of hydrogen present, was changed from 25 mol. % to 0.7 mol. %. At the same time, the temperature of hydrogenation was lowered from 90° to 60° C. to prevent excessive hydrogenation.

The composition of the product thus obtained is described under "Product B" in Table 1.

TABLE 1

Feed Composition (mol. %)	Product Composition (mol. %)	
	Product A	Product B
Propane and Propylene 2.8	2.7	2.7
Isobutane 4.7	4.7	4.8
n-Butane 9.5	9.6	9.5
Isobutene 43.1	43.1	43.0
1-Butene 24.7	25.1	25.1
2-Butene 14.0	14.8	14.9
1,3-Butadiene 1.2	(205 p.p.m.)	(113 p.p.m.)

As is apparent from Table 1, the content of 1-butene in Product B is the same as that in Product A. This clearly proves that the double bond migration during the selective hydrogenation is effectively prevented when the content of carbon monoxide based on the hydrogen is changed from 25 mol. % to 0.7 mol. % after the initial stage of the reaction.

COMPARATIVE EXAMPLE 1

The selective hydrogenation was carried out using the same feed, catalyst and reaction conditions as those used in Example 1 except that hydrogen free from carbon monoxide was utilized. The composition of the butene feed and the compositions of the hydrogenation products, "Product A" obtained after 2 hours from the start of the reaction, and "Product B" obtained after 4 days, are shown in Table 2.

TABLE 2

Feed Composition (mol. %)	Product Composition (mol. %)	
	Product A'	Product B'
Propane and Propylene 2.8	2.0	2.1
Isobutane 4.7	6.7	6.7
n-Butane 9.5	13.1	13.0
Isobutene 43.1	43.2	43.1
1-Butene 24.7	3.8	3.8
2-Butene 14.0	31.1	31.2
1,3-Butadiene 1.2	0.05	0.05

As apparent from Table 2, almost all of the 1-butene undergoes double bond migration and is converted to 2-butene during selective hydrogenation when carbon monoxide is not present in the reaction system.

EXAMPLE 2

The procedure of Example 1 was repeated except that the hydrocarbon feed employed was a C₄-fraction having the composition shown in Table 3, which was produced by naphtha steam cracking. The reaction was carried out at a temperature of 80° C. under a pressure of 25 kg/cm², and the rate of hydrogen containing 5 mol. % carbon monoxide was 500 liters (N.T.P.)/hr.

The composition of the product obtained after 2 hours from the start of the reaction is shown under "Product C" in Table 3.

After 15 days from the start of the reaction, the content of carbon monoxide based on hydrogen was changed from 5 mol. % to 0.5 mol. % and the reaction temperature was lowered from 80° to 60° C. to prevent excessive hydrogenation.

The composition of product thus obtained is also given under "Product D" in Table 3.

TABLE 3

Feed Composition (mol. %)	Product Composition (mol. %)	
	Product C	Product D
Isobutene 7.1	7.1	7.2
n-Butane 6.0	6.1	6.1
Isobutene 24.1	25.3	25.0
1-Butene 13.8	23.0	23.3
2-Butene 8.0	38.5	38.4
1,3-Butadiene 39.2	(94 p.p.m.)	(88 p.p.m.)
Vinyl acetylene 1.8	(0 p.p.m.)	(0 p.p.m.)

EXAMPLE 3

The procedure of Example 1 was repeated except that the reaction was carried out at a temperature of 100° C. under a pressure of 15 kg/cm², and the rate of hydrogen containing 5 mol. % carbon monoxide was 50 liters (N.T.P.)/hr. A nickel-containing hydrogenation catalyst containing 1.0 % by weight of nickel supported on alumina was used in place of palladium-alumina catalyst.

The composition of the product obtained after two hours from the start of the reaction is shown under "Product E" in Table 4.

After 30 days from the start of the reaction, the content of carbon monoxide was changed from 5 mol. % to 0.5 mol. % and the temperature of hydrogenation was lowered from 100° to 70° C. to prevent excessive hydrogenation.

The composition of the product thus obtained is given under "Product F" in Table 4.

TABLE 4

Feed Composition (mol. %)	Product Composition (mol. %)	
	Product E	Product D
Propane and Propylene	2.8	2.8
Isobutane	4.8	4.7
n-Butane	9.5	9.6
Isobutene	43.6	43.2
1-Butene	25.4	25.4
2-Butene	13.9	14.3
1,3-Butadiene	(52 p.p.m.)	(44 p.p.m.)

EXAMPLE 4

The procedure of Example 1 was employed except that the reaction was carried out at a temperature of 100° C. under a pressure of 15 kg/cm².

The composition of the product obtained after 2 hours from the start of the reaction is given under "Product G" in Table 5.

After 30 days from the start of the reaction, the content of carbon monoxide based on hydrogen present was changed from 25 mol. % to 2.0 mol. % and the reaction temperature was lowered from 90° to 80° C. to prevent excessive hydrogenation.

After 60 days from the start of the reaction, the content of carbon monoxide was further changed from 2.0 mol. % to 0.5 mol. % and the reaction temperature was lowered from 80° to 60° C.

The compositions of the former and the latter product are given under "Product H" and "Product K," respectively, in Table 5:

TABLE 5

Feed Composition (mol. %)	Product Composition (mol. %)		
	G	H	K
Propane and Propylene	2.7	2.8	2.7
Isobutane	4.7	4.7	4.7
n-Butane	9.6	9.2	9.6
Isobutene	43.2	43.7	43.1
1-Butene	25.2	24.9	25.3
2-Butene	14.6	14.7	14.6
1,3-Butadiene	(85 p.p.m.)	(71 p.p.m.)	(57 p.p.m.)

Having now described the present invention with particu-

larity, it is readily apparent that various changes and modifications may be made without departing from the scope thereof.

What is claimed is:

1. A process for the selective hydrogenation of at least one member, having at least four carbon atoms in the molecule, selected from the group consisting of a polyolefin, an alkyne, and alkenyne, and mixtures thereof in a hydrocarbon mixture containing at least one mono-olefin having at least four carbon atoms in the molecule, which comprises contacting said hydrocarbon mixture with a copper-free hydrogenation catalyst comprising a member selected from the group consisting of palladium and nickel under selective hydrogenation conditions in the presence of hydrogen and carbon monoxide of 1-50 mol. %, based on the hydrogen, during the initial stage of the reaction and thereafter lowering the content of carbon monoxide to a range of 0.05-1 mol. %, based on the hydrogen, said process preventing double bond migration of the mono-olefin.

2. The process of claim 1, wherein the carbon monoxide is present in an amount of from 5 to 30 mol. % based on the hydrogen during the initial stage of the reaction.

3. The process of claim 1, wherein the content of carbon monoxide is lowered after the total amount of carbon monoxide added into the reaction system comes to at least 0.05 moles per gram of the hydrogenation catalyst.

4. The process of claim 1, wherein the content of carbon monoxide is lowered after the total amount of carbon monoxide added into the reaction system comes to at least 0.1-20 moles per gram of the hydrogenation catalyst.

5. The process of claim 1, wherein the content of carbon monoxide is lowered after the total amount of carbon monoxide added into the reaction system comes to at least 0.2-10 moles per gram of the hydrogenation catalyst.

6. The process of claim 1, wherein the hydrogenation is carried out at a temperature of from 20° to 250° C.

7. The process of claim 1, wherein the hydrogenation is carried out under a pressure of from atmospheric to 50 kg/cm².

8. The process of claim 1, wherein the hydrocarbon mixture is a mixture of compounds having from 4 to 16 carbon atoms in the molecule.

9. The process of claim 8, wherein the hydrocarbon mixture is a C₄ fraction.

10. The process of claim 8, wherein the hydrocarbon mixture is a C₅ fraction.

11. The process of claim 1, wherein the hydrocarbon mixture contains paraffinic hydrocarbons.

12. The process of claim 1, wherein the catalyst is supported on a carrier.

13. The process of claim 12, wherein the catalyst is palladium supported on alumina.

14. The process of claim 12, wherein the catalyst is nickel supported on alumina.

15. The process of claim 1, wherein the amount of palladium catalyst present ranges from 0.005-3.0% by weight.

16. The process of claim 1, wherein the amount of nickel catalyst present ranges from 1-40% by weight.

17. The process of claim 1, wherein the amount of hydrogen per total mole of polyunsaturated hydrocarbons ranges from 1-20,000 moles.

18. The process of claim 1, wherein the liquid hourly space velocity of the hydrocarbon feed ranges from 0.1 to 40.0.

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