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ISOMERIZATION OF 1-OLEFINS TO 2-OLEFINS

James W. Garner and Bruce C. Benedict, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Isomerization of 1-olefins to 2-olefins over catalysts of the noble metals of Group VIII on alumina in the presence of hydrogen. Sulfur compounds effectively reduce hydrogenation of the olefins while maintaining double bond isomerization activity of the catalyst.

This invention relates to a process for the catalytic double bond isomerization of olefinic hydrocarbons. More specifically it relates to a process for the double bond isomerization of olefins in the presence of hydrogen wherein the hydrocarbon mixture containing the olefin further contains sulfur compounds, naturally present or added, so as to effectively reduce loss of olefins by hydrogenation while yet permitting maximum double bond isomerization activity of the catalyst.

The process of the present invention is applicable to the treatment of various unsaturated hydrocarbons, particularly to the unsaturated hydrocarbons having a terminal double bond between two non-tertiary carbon atoms. The term "non-tertiary" indicates that the double-bonded carbon atoms are non-tertiary, although the hydrocarbon may contain tertiary carbon atoms remote from the double bonded carbon atoms. The radicals attached to such tertiary carbon atoms may be of alkyl, aryl, or aralkyl type.

The particular unsaturated hydrocarbons to which this invention is most applicable are termed 1-olefins and have a chain of at least four carbon atoms. Examples of such hydrocarbons include butene-1, pentene-1, hexene-1, and higher homologues; 3-methyl pentene-1, 4-methyl hexene-1, 4-phenyl hexene-1, and the like. Of course, process stream hydrocarbon mixtures can be subjected to this invention where such streams contain mixtures of various 1-olefins, or various 1-olefins plus saturated hydrocarbons.

Where the hydrocarbon feed stream to be subjected to double bond isomerization additionally contains unsaturated hydrocarbons such as diolefins or polyolefins, or acetylenic impurities and the like, pretreatment by means known to the art should be employed to remove such impurities. If not removed beforehand, such impurities tend to polymerize during and to interfere with double bond isomerization, or to be converted during the process to undesirable products or polymers.

Although the presence of saturated hydrocarbons corresponding to the olefins, such as butanes, pentanes, hexanes, and the like, is not detrimental, the saturated hydrocarbons do have a diluting action on the treated olefins. This invention may be practiced either in the presence or absence of such diluting saturated hydrocarbons, depending upon the overall concentration of olefin present or desired after the isomerization process.

It is the method of this invention to provide a process of isomerizing 1-olefins to 2-olefins or internal olefins, such as isomerizing butene-1 to butene-2, over a single catalyst, the isomerization being performed without interference by the presence of, and surprisingly with the effective aid of, sulfur compounds.

Heretofore, sulfur-containing compounds in a hydro-

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carbon feed stream have been considered as catalyst poisons, severely poisoning isomerization catalysts so as to greatly reduce and prevent effectiveness of double bond isomerization. Extensive preliminary processes have been required to essentially eliminate the sulfur compounds before the isomerization step could proceed effectively and successfully. The advantages of the present invention over prior art processes include simplification of process equipment, simplification of operation, minimization of plant investment, and reduced operating costs.

By the method of this invention, there is provided a process for isomerizing a monoolefinic 1-olefin hydrocarbon in a hydrocarbon stream also containing sulfur compounds, the process comprising contacting the hydrocarbon stream containing the sulfur compounds at elevated temperature in the presence of hydrogen with a catalyst to convert at least a portion of the 1-olefins to internal olefins or 2-olefins. Further, by the method of this invention, there is provided a process for adding sulfur-containing compounds to a hydrocarbon stream containing 1-olefins, and thereafter contacting the hydrocarbon stream in the presence of hydrogen with a catalyst to convert at least a portion of the 1-olefins to internal olefins or 2-olefins.

Specifically, by the method of this invention, the sulfur compounds, either present naturally in the hydrocarbon stream or added as a component to a hydrocarbon stream otherwise substantially free of sulfur compounds, affect the properties of the catalysts of the process so that effective double bond isomerization of the 1-olefin is obtained while the otherwise associated hydrogenation activity of the catalysts for olefins is substantially suppressed. Therefore, by this invention, loss of olefins to formation of saturated hydrocarbons by the associated hydrogenation activity of the catalysts is substantially avoided, thus effecting considerable savings in olefin, avoiding loss of the active olefin feedstock to saturated hydrocarbons, and achieving valuable savings in materials. These advantages are in addition to the large reduction in capital investment attained by reduction in process equipment through elimination of sulfur-removing treating steps as disclosed hereinabove.

Accordingly, it is an object of this invention to provide an improved olefin double bond isomerization process and improved olefin double bond isomerization catalysts.

It is also an object of this invention to provide an olefin double bond isomerization process in which the activity of the catalysts is beneficially affected by a novel method of treatment.

Additional objects and advantages of this invention will become apparent from the descriptions and examples.

This invention can be carried out in any of the usual processing methods and sequences, including series or parallel flows of reactants and similar modifications and adaptations generally applicable to hydrocarbon processing. Similarly, provision can be made for control of process conditions by the usual instrumentation.

A typical hydrocarbon feed composition suitable for the process of this invention is a feed stream containing saturated hydrocarbons, isobutylene, butadiene, butene-2 in both the cis and trans forms, butene-1 (the component desired to be isomerized to butene-2), and minor amounts of diolefins. Another typical hydrocarbon feed stream is one containing propane, propylene, butanes, butenes, 3-methyl butene-1, 2-methyl butene-1, 2-methyl butene-2, and minor amounts of diolefins such as 1,3-butadiene. The process stream will either contain sulfur compounds, organic or inorganic in type, one or more, or a sulfur-containing compound, one or more, will be added to the process stream, according to this invention.

Catalysts suitable for use in the process of this invention include the noble metals of Group VIII of the Periodic

Table of Elements, as listed in the Handbook of Chemistry and Physics, published by the Chemical Rubber Company, in the 49th edition (1969), page B-3. The catalysts intended to be included in the group of noble metals of Group VIII specifically are ruthenium, rhodium, palladium, osmium, iridium, and platinum. This invention is effective with the catalysts listed, and not with the other metals of Group VIII, namely, iron, cobalt and nickel. Iron, cobalt, and nickel appear to undergo direct reactions with sulfur compounds to form various metal sulfides. The noble metals of Group VIII do not react directly with sulfur compounds contained in the feed stream under the temperatures of this invention, though their activity is distinctively and surprisingly affected by the process of this invention.

Any of the usual catalyst supports can be employed, such as alumina (preferred), silica alumina, glass beads, and carbon. Both pelleted and spherical form catalysts are satisfactory.

A preferred catalyst is palladium on a carrier, the carrier preferably being alumina. The catalyst should contain from 0.005 to 1.0 percent palladium on alumina, preferably about 0.01 to about 0.1 weight percent palladium on alumina. The alumina carrier is of a controlled pore diameter to contain about 41.5 weight percent aluminum. A suitable catalyst weighs about 40 to about 52 pounds per cubic foot, has a surface area of about 340 to about 350 square inches per gram, a pore volume of about 0.50 to about 0.60 ml. per gram, and a pore diameter of about 60 to about 70 Å.

A commercial catalyst satisfactory for use in this invention is manufactured by Catalysts and Chemicals, Inc., Louisville, Kentucky, designated as catalyst C-31 and described in Bulletin No. C-31-053. The commercial catalyst contains about 0.05 weight percent palladium on alumina.

Another commercial catalyst satisfactory for use in this invention is manufactured by the Girdler Corporation, Louisville, Kentucky, designated as catalyst G-55 and described in Data Sheet G-55-562, and contains about 0.03 weight percent palladium on alumina.

The process is conducted at a reaction temperature of about 275 to 500° F., preferably 325-375° F. and such temperature range is critical to the process of this invention. Lower temperatures are ineffective. Higher temperatures tend to shift the catalytic equilibrium produced between the 1-olefin (feed stream) and the 2-olefin (desired product) away from the 2-olefin and toward the 1-olefin, thus reducing the yield of the desired 2-olefin.

This invention can be most effectively practiced at relatively low pressure conditions while maintaining the hydrocarbon most preferably in the vapor phase, although liquid phase operation can be used. Pressures employed are from about 15 to about 250 p.s.i.g., preferably from about 50 to about 160 p.s.i.g. Hourly space velocities, VHSV, are maintained from about 100 to 10,000, preferably from about 1,000 to about 2,000, based on standard conditions.

Hydrogen is required in the practice of this invention, preferably being mixed with the hydrocarbon stream prior to contacting the stream with the catalyst, preferably after vaporization of the hydrocarbon. The hydrocarbon can be added undiluted, or added diluted with an inert gas. The hydrogen is necessary to effect double bond isomerization of the 1-olefin with the catalysts of our process. The hydrogen is added in amounts from 0.1 to 5.0 mol percent, preferably in amounts of about 0.2 to about 1.2 mol percent.

The process of this invention is applicable to a hydrocarbon feed stream containing the 1-olefin of which it is desired to convert the double bond to an internal position and wherein in the stream is also found, or is added, a sulfur compound. The sulfur compounds can be any naturally occurring organic or inorganic sulfur compound that can be conveniently added, and may be in the form

of gaseous, liquid, or solid materials under normal temperatures and pressures. Examples of suitable sulfur compounds include: sulfides, such as hydrogen sulfide, alkali and alkaline earth metal sulfides; thioalcohols (mercaptans) and alkali and alkaline earth metal salts thereof; thioethers; thioaldehydes; thioketones; disulfides, both organic and inorganic, such as alkali and alkaline earth disulfides; thionacids; thiolacids; dithioacids; thiourea; isothiocyanates; dithiocarbonates (xanthates); or the like. In any of which compound the organic component of the compound may have up to about 10 carbon atoms for alkyl, up to about 18 carbon atoms for cyclic, and be of alkyl, aryl, alkaryl, aralkyl type, and include various substituents on the chain or ring including halide, amino, carboxy, hydroxy, and the like.

The organic sulfur compound can be added as a gas, as a liquid, as a vaporized solid, as a solution, in undiluted form, or in diluted form, using any convenient means known to the art to add a minor amount of such a material to a hydrocarbon feed stream.

This invention, carried out within the ranges as described hereinbefore, is illustrated by the following examples. The examples, adapted to the isomerization of butene-1 to butene-2, should be considered as illustrative of the general applicability of the process to the feedstocks previously discussed, and without being limitative of the invention.

EXAMPLE I

A hydrocarbon stream was isomerized under the operating conditions indicated below, using a palladium on alumina catalyst of the type as described hereinbefore, at a temperature of 250° F., and in the absence of a sulfur compound. It will be noted that butene-1 is converted to butene-2 under these conditions, but that, however, a high consumption of hydrogen is shown by the formation of paraffins.

RUN NO. A

Process pressure	-----p.s.i.g.---	110
Process temperature	-----° F.---	250
VHSV	-----	1,000
H ₂ addition mols per 100 mols of hydrocarbon	---	1.18
Sulfur compound	-----	none

	Stream analysis (Mol percent unless noted)	
	Feed stream	Effluent composition
Hydrogen	(1)	Nil
Propylene	12.8	12.42
Propane	1.36	1.74
iso-Butane	52.9	51.9
n-Butane	0.30	1.00
Butene-1	13.9	3.4
Butene-2	19.5	29.3
Total C ₄	0.24	0.24
Butene-2/butene-1 ratio	1.4	8.5
Butene-1 conversion	-----	2 75
Paraffins formed, mols per 100 mols of Hydrocarbon	-----	1.07
Percent of H ₂ consumed forming paraffin	-----	2 91

¹ Feed Stream composition given on a hydrogen-free basis.

² Percent

The above example shows that at a temperature of 250° F. and in the absence of the sulfur compound that the catalyst is active both as a double bond isomerization catalyst and as a hydrogenation catalyst.

EXAMPLE II

An embodiment of this invention was carried out with a feed stream containing butene-1 so as to isomerize the butene-1 to butene-2, using the same catalyst and temperature as in Example I, except that the feed stream here contained a sulfur compound.

RUN NO. B

Process pressure -----p.s.i.g.----- 110
 Process temperature -----° F----- 250
 VHSV ----- 1,000
 H₂ addition mols per 100 mols of hydrocarbon --- 1.18
 Sulfur compound ----- Present

	Stream analysis (Mol percent unless noted)	
	Feed stream	Effluent composition
Hydrogen.....	(1)	1.13
Ethane.....	26.59	26.27
Propylene.....	10.8	10.66
Propane.....	0.08	10.0
iso-Butane.....	0.03	0.05
n-Butane.....	0.03	0.03
iso-Butylene.....	3.7	3.64
Butene-1.....	10.4	10.4
Butene-2.....	14.3	14.1
iso-Pentane.....	0.06	0.06
n-Pentane.....	29.2	28.8
3-methyl butene-1.....	2.51	2.50
2-methyl butene-1.....	0.20	0.20
2-methyl butene-2.....	2.10	2.06
Butene-2/butene-1 ratio.....	1.4	1.4
Butene-1 conversion.....		20
3-methyl butene-1 conversion.....		20
Paraffins formed, mols per 100 mols of hydrocarbons.....		0.04
H ₂ consumed in forming paraffins.....		23

¹ Feed Stream composition given on a hydrogen-free basis.

² Percent.

From the above example it will be observed that the presence of the sulfur compound at a temperature of 250° F. did dampen the hydrogenation activity toward the 1-olefins but also effectively and undesirably destroyed the double bond isomerization properties of the catalyst.

EXAMPLE III

Process streams similar to that used in Example II above were subjected to the operating conditions as described below for the purpose of isomerizing butene-1 to butene-2, with the process feed stream containing a sulfur compound, and, in contrast to Example II, the runs being made at temperatures of 310–311° F., thus within the process of this invention.

RUNS NOS. C, D, AND E

	Run C	Run D	Run E
Process Pressure, p.s.i.g.....	110	110	110
Process Temperature, ° F.....	310	310	311
VHSV.....	1,000	1,000	1,000
H ₂ addition mols per 100 mols of hydrocarbon.....	1.18	1.18	1.18
Sulfur Compound.....	(1)	(2)	(2)

¹ Present.

² CH₃SH, 10 mol p.p.m.

³ H₂S, 19 mol p.p.m.

	Stream analysis (Mol percent unless noted)	
	Feed stream	Effluent composition
	Runs C and D	Run C Run D
Hydrogen.....	(1)	1.11 1.14
Ethane.....	24.88	24.6 24.6
Propylene.....	10.8	10.67 10.69
Propane.....	0.13	0.14 0.12
iso-Butane.....	0.05	0.07 0.08
n-Butane.....	0.06	0.08 0.06
iso-Butylene.....	3.9	3.84 3.83
Butene-1.....	10.7	6.5 8.2
Butene-2.....	14.7	18.6 17.0
iso-Pentane.....	0.06	0.07 0.06
n-Pentane.....	29.8	29.46 29.36
3-methyl butene-1.....	2.55	1.16 1.90
2-methyl butene-1.....	0.29	0.34 0.26
2-methyl butene-2.....	2.08	3.36 2.7
Butene-1/butene-2 ratio.....	1.4	2.9 2.1
Butene-1 conversion.....		38 23
3-methyl butene-1 conversion.....		54 25
Paraffins formed, mols per 100 mols of hydrocarbon.....		0.06 0.03
H ₂ consumed in forming paraffins.....		5 3

¹ Feed stream composition given on a hydrogen-free basis.

	Stream analysis (Mol percent unless noted)	
	Feed stream, Run E	Effluent composition, Run E
Hydrogen.....	(1)	1.10
Ethane.....	24.56	26.2
Propylene.....	11.0	10.86
Propane.....	0.09	0.11
iso-Butane.....	0.04	0.06
n-Butane.....	0.05	0.07
iso-Butylene.....	3.9	3.84
Butene-1.....	10.0	6.9
Butene-2.....	4.6	17.5
iso-Pentane.....	0.06	0.07
n-Pentane.....	28.8	28.45
3-methyl butene-1.....	2.64	1.94
2-methyl butene-1.....	0.16	0.1
2-methyl butene-2.....	2.10	2.8
Butene-2/butene-1 ratio.....	1.5	2.5
Butene-1 conversion.....		30
3-methyl butene-1 conversion.....		26
Paraffins formed, mols per 100 mols of hydrocarbon.....		0.07
H ₂ consumed in forming paraffins.....		6

¹ Feed stream composition given on a hydrogen-free basis.

The data given in Example III above illustrate the effect of the presence of sulfur compounds in the feed stream in combination with elevation of the process temperature to 310–311° F. In Run C the specific sulfur compound was not identified but was positively present; in Run D the sulfur compound was CH₃SH present at 10 mol p.p.m.; in Run E the sulfur compound was H₂S present at 19 mol p.p.m. Example III data above show that the high effectiveness of the combination of the presence of a sulfur compound plus the elevation in temperature to 310–311° F. effectively permits double bond isomerization while equally effectively suppressing hydrogenation activity of the catalyst. The runs of Examples III and IV also demonstrate effectiveness of both organic and inorganic sulfur to this invention.

EXAMPLE IV

	Run F	Run G
Pressure, p.s.i.g.....	110	110
Feed and Bath Temp., ° F.....	372	375
VHSV.....	1,000	1,000
H ₂ addition, mols per 100 mols of Hydrocarbon.....	1.18	1.18
Sulfur compound.....	(1)	(2)

¹ CH₃SH, 10 mol p.p.m.

² H₂S, 19 mol p.p.m.

	Stream analysis (Mol percent unless noted)			
	Feed stream		Effluent composition	
	Run F	Run G	Run F	Run G
Hydrogen.....	(1)	(1)	1.12	1.09
Ethane.....	24.88	26.56	24.6	26.27
Propylene.....	10.8	11.0	10.67	10.85
Propane.....	0.13	0.09	0.14	0.12
iso-Butane.....	0.05	0.04	0.06	0.05
n-Butane.....	0.06	0.05	0.08	0.08
iso-Butylene.....	3.9	3.9	3.85	3.85
Butene-1.....	10.7	10.0	5.1	5.5
Butene-2.....	14.7	14.6	20.0	18.9
iso-Pentane.....	0.06	0.06	0.07	0.07
n-Pentane.....	29.8	28.8	29.46	28.49
3-methyl butene-1.....	2.55	2.64	0.70	1.41
2-methyl butene-1.....	0.29	0.16	0.21	0.16
2-methyl butene-2.....	2.08	2.10	3.94	3.34
Butene-2/butene-1 ratio.....	1.4	1.5	3.9	3.4
Butene-1 conversion.....			52	44
3-methyl butene-1 conversion.....			72	46
Paraffins formed, mols per 100 mols of hydrocarbon.....			0.05	0.08
H ₂ consumed in forming paraffins.....			4	7

¹ Feed stream composition given on a hydrogen-free basis.

The above example further confirms the effectiveness of addition of various types of sulfur compounds, at various addition amounts, and at somewhat higher temperatures still within the range of the invention, showing even further improvement in percent of butene-1 conversion while yet maintaining extremely low percent of hydrogen consumption to formation of paraffins, thus illustrating the effectiveness of the sulfur compounds in

suppressing hydrogenation activity of the catalyst while yet maintaining full double bond isomerization activity.

The examples given in the disclosure show primarily conversion of butene-1 to butene-2; these examples are not to be considered as limiting the feedstock to which the present invention is applicable.

Reasonable variations and modifications are within the scope of the disclosure of this invention and would be made by those skilled in the art without departing from the scope and spirit of the present invention.

That which is claimed is:

1. A method of treating a catalyst selected from the noble metals of Group VIII, said catalysts having both hydrogenation and double bond isomerization activity toward 1-olefins, which comprises contacting said catalyst with a feed stream containing said 1-olefins and at least one sulfur-containing compound at from about 275° to about 500° F. and thereby substantially affecting the hydrogenation properties of said catalyst while maintaining substantially the double bond isomerization properties of said catalyst.

2. A process for treating a hydrocarbon stream to isomerize 1-olefins contained in said stream to 2-olefins, the said stream further containing sulfur compounds tending to cause loss of isomerization properties of an isomerization catalyst selected from the noble metals of Group VIII, which comprises:

- (a) mixing said hydrocarbon stream in the fluid state with H₂,
 - (b) heating the mixture of hydrocarbon stream containing sulfur compounds and H₂ to a temperature at from about 275° to about 500° F. sufficient to maintain double bond isomerization properties of the catalyst while permitting the sulfur compounds to substantially decrease the hydrogenation properties of said catalyst,
 - (c) contacting the heated mixture with said catalyst, thereby substantially decreasing the hydrogenation properties of the said catalyst and thereby substantially preventing loss of olefins by hydrogenation, and thereby maintaining maximum double bond isomerization of the said 1-olefins to 2-olefins,
 - (d) recovering the said 2-olefins as a product.
3. The process of claim 2 wherein the catalyst contains from about 0.005 to about 1.0 percent palladium on alumina.
4. The process of claim 2 wherein step (c) is followed by:
- (d) cooling the isomerized mixture,
 - (e) conducting the cooled mixture to a separation zone,
 - (f) separating the H₂ from the isomerized mono-olefins,
 - (g) recycling the separated H₂ from step (f) to step (a), and
 - (h) recovering the isomerized monoolefin from step (f) as a product.
5. The process of claim 2 wherein the said sulfur-

containing compound in step (b) is added directly to the reaction zone.

6. The process of claim 2 wherein the said hydrocarbon stream already contains a sulfur-containing compound and wherein in step (b) the amount of sulfur-containing compound there admixed is reduced accordingly.

7. The process of claim 6 wherein the amount of sulfur-containing compound added in step (b) is from about 1 to about 50 mol p.p.m. as sulfur.

8. A method of treating a catalyst selected from the noble metals of Group VIII, said catalysts having both double bond isomerization and hydrogenation properties in contacting a stream containing 1-olefins, which comprises:

- (a) admixing with said stream at least one sulfur-containing compound and with hydrogen,
- (b) heating the stream from step (a) to a temperature at from about 275° to about 500° F. sufficient to maintain double bond isomerization properties of said catalyst while substantially decreasing the hydrogenation properties of said catalyst,
- (c) contacting the said catalyst with said heated mixture from step (b), thereby substantially decreasing the hydrogenation properties of said catalyst while substantially maintaining the double bond isomerization properties of said catalyst.

9. The method of claim 8 wherein the catalyst contains from about 0.005 to about 1.0 weight percent palladium on alumina.

10. The method of claim 8 wherein the activity of the catalyst is affected by contacting with said stream containing at least one sulfur-containing compound at from about 325 to about 375° F.

11. The process of claim 8 wherein the said hydrocarbon stream already contains a sulfur-containing compound and wherein in step (a) the amount of sulfur-containing compounds therein admixed is reduced accordingly.

12. The method of claim 8 wherein the amount of at least one sulfur-containing compound added in step (a) is from about 1 to about 50 mol p.p.m. as sulfur.

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DELBERT E. GANTZ, Primary Examiner

VERONICA O'KEEFE, Assistant Examiner