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(54) **Title**: CATALYTIC ISOMERISATION OF LINEAR OLEFINIC HYDROCARBONS

(57) **Abstract**: Gallium-niobium oxide catalysts are disclosed herein for converting linear olefinic hydrocarbons to branched olefinic hydrocarbons through isomerisation, the latter being capable for use fuel for their desirable properties.

CATALYTIC ISOMERISATION OF LINEAR OLEFINIC HYDROCARBONS

Cross Reference to Related U.S. Application

[0001] This application claims priority to U.S. Provisional Application No. 61/469,384, titled "Catalytic isomerisation of linear, olefinic hydrocarbons," filed on March 30, 2011.

FIELD OF INVENTION

[0002] The invention relates to catalytic isomerisation of linear olefinic hydrocarbons to branched isomers, wherein under certain conditions the branched isomers provide advantageous properties compared to their linear analogs.

BACKGROUND

[0003] Hydrocarbons are an energy source for internal combustion engines, for turbines in jet aircraft, and for other kinds of engines, as well as for other applications that require a source of fuel. For example, hydrocarbon fuels like gasoline are made up of hydrocarbons having about 4-9 carbon atoms in their molecular structure. Kerosene fuels (about 9-15 carbon atoms), jet fuels (9-15 carbon atoms), and diesel fuels (12-20 carbon atoms) are other examples. Lubricant base oils, which have a relatively higher viscosity index than the other examples, typically have 22-35 carbon atoms.

[0004] For some time, hydrocarbon fuels, in addition to other petrochemical products, have been obtained from crude petroleum oil through a series of conventional steps. Such steps include, but are not necessarily limited to, distillation followed by additional refining. Attempts are being made, however, to produce hydrocarbon fuels from alternative, renewable sources, including but not limited to feedstocks of biological origin. Moreover, because of their similar chemical properties and functional properties, some hydrocarbon fuels that are

from alternative, renewable sources are compatible with and, therefore, acceptable for use with, the kinds of engines for which petroleum-derived hydrocarbon fuels are intended.

[0005] More specifically, hydrocarbon fuels, which are from alternative, renewable sources other than petroleum, include those products which are obtained from catalytic isomerisation of linear, olefinic hydrocarbons, as described and taught herein. In some cases, such products are capable of being stored and transported through existing infrastructure (e.g., storage tanks and pipelines) as with petroleum-derived hydrocarbon fuels. This improves the feasibility of using such products as replacements for petroleum-derived hydrocarbon fuels in their applications as fuels.

[0006] The words "linear" and "branched" refer to the molecular structure of a hydrocarbon's skeletal chain. In some applications relating to fuels, lubricants, and petrochemical products, the hydrocarbons are linear. In other applications, the hydrocarbons are branched. In some applications, including some in which hydrocarbons are primary constituents for gasoline, kerosene fuels, jet fuels, and diesel fuels, the use of branched hydrocarbons is advantageous over the use of their linear hydrocarbon analogs.

[0007] For example, methylhexane is the branched analog of normal heptane. Methylhexane, with an octane number of 44, has a higher octane number than normal heptane, which has an octane number of zero. Branched hydrocarbons with about 9-15 carbon atoms, e.g., when used as kerosene or jet fuel, have lower freezing points and lower pour points than their linear analogs. In certain cold temperature conditions, such properties are advantageous when compared to the properties of linear hydrocarbons having the same number of carbons. Likewise, branched hydrocarbons used in diesel fuels, which are typically 12-20 carbon atoms in length, have lower freezing points and lower pour points than their linear analogs. In the case of lubricant base oils containing 20-35 carbon atoms,

branched analogs have lower freezing points and higher viscosity indices than their linear counterparts.

[0008] Besides the difference between linear branched, another consideration is whether hydrocarbons contained in fuels, lubricants, and petrochemical products are paraffinic (saturated) or olefinic (unsaturated). Under certain conditions, such as cold temperature, olefinic hydrocarbons provide various advantages over the use of paraffinic hydrocarbons containing the same number of carbon atoms, including but not limited to lower freezing points and lower pour points.

[0009] Branched olefinic hydrocarbons, e.g., of the kind which can be used as replacements for petroleum-derived hydrocarbon fuels, do not occur naturally in large supply. However, starting materials for the production of branched olefinic hydrocarbons, for example biomass raw materials, are found naturally in relatively large supply. Accordingly, such starting materials are considered to be an alternative, renewable source of hydrocarbon fuels. For example, the lipid portions of plant oils, animal fats, animal oils and algae oils are a ready source of triglycerides, which are converted to carboxylic acids through methods known to persons of ordinary skill in the art, such as hydrolysis that produces carboxylic acids and glycerine. In turn, various methods are known to persons of ordinary skill in the art for the conversion of carboxylic acids to linear olefinic hydrocarbons, where the carboxylic acid is of the formula R-COOH and R is an olefinic hydrocarbon group. These include hydrodeoxygenation, or (alternatively) decarboxylation, or (alternatively) decarbonylation. If the carboxylic acid starting materials are unsaturated, then the resulting hydrocarbon will be a linear, olefinic hydrocarbon. For example, oleic acid ($C_{17}H_{33}COOH$) is a monounsaturated fatty acid found in olive oil. The above-mentioned oxygen-removal methods convert oleic acid to heptadecene or octadecene, which are linear, olefinic hydrocarbons.

[00010] Another known method is the conversion of linear, paraffinic hydrocarbons to linear, olefinic hydrocarbons by dehydrogenation over a metal catalyst, such as platinum, palladium, or nickel, or a combination of those. Regardless of how they are produced, the isomerisation of linear, olefinic hydrocarbons to branched olefinic hydrocarbons has been performed either at high temperatures or over solid acid catalysts, such as a zeolite or silicoalumina catalyst. However, the isomerisation reactions under such conditions, and/or with the use of such catalysts, generally produce a relatively high percentage of shorter-chain, lower molecular weight hydrocarbon products due to hydrocracking. Accordingly, there is a need for a suitable catalyst and / or catalytic process for the isomerisation of branched olefinic hydrocarbons from linear, olefinic hydrocarbons. There is also a need for such a catalyst and / or catalytic process with suitable selectivity for isomerisation, as opposed to reactions that may be less desirable in certain situations, such as hydrocracking.

SUMMARY OF INVENTION

[00011] The present embodiments provide suitable catalysts and / or catalytic processes for the isomerisation reaction of linear, olefinic hydrocarbons to branched olefinic hydrocarbons, with suitable selectivity for isomerisation, as opposed to reactions that may be less desirable in certain situations, such as hydrocracking. In some embodiments, the isomerisation reaction occurs over mixed gallium-niobium oxide catalysts, and comprises the steps of contacting linear olefinic hydrocarbon reactants with the catalyst and isolating the branched olefinic hydrocarbon products through methods known to those skilled in the art.

MULTIPLE EMBODIMENTS AND ALTERNATIVES

[00012] Like their branched analogs, linear olefinic hydrocarbons do not occur naturally in abundant supply. However, various methods discussed above exist for obtaining linear olefinic hydrocarbons from sources that are found naturally in relatively large supply. The present embodiments convert linear olefinic hydrocarbons to their branched olefinic

hydrocarbons through catalytic isomerisation. The approach recognizes that, regardless of which route or process as discussed in the Background is employed, linear hydrocarbons (both paraffinic and olefinic) are capable of being produced or obtained from sources that are in relatively large supply.

[00013] In some embodiments, the linear olefinic hydrocarbon starting materials and the branched products have four or more carbon atoms, and the number of carbons in the branched products equals the number of carbons in the starting materials. In some embodiments, the starting materials and products have no more than 35 carbons, and the number of carbons in the branched products is equal to the number of carbons in the starting materials. The process comprises (1) obtaining, or producing, a supply of at least one linear, olefinic hydrocarbon; (2) selecting, or preparing, a catalyst; and (3) contacting the at least one linear, olefinic hydrocarbon with the catalyst, under conditions as described herein. In some embodiments, the reaction is carried out at a temperature between 150 – 450 ° C.

[00014] Among other factors, the selectivity for branched olefinic hydrocarbon products is influenced by the number of acid sites on the catalyst, and the strength of the acid sites. Generally, if all other factors are substantially equal, then catalysts with relatively high acidity are more prone to hydrocracking than those catalysts with lower acidity.

[00015] In some embodiments, the reaction catalyst is a mixed oxide of gallium-niobium, prepared as follows. An inorganic precursor is dissolved in alcohol, for example one chosen from the group methanol, ethanol, propanol, isopropanol, butanol, isobutanol, and tertiary butanol. A structure directing agent is dissolved in an alcohol, for example ethanol or isopropanol. In some embodiments, the structure directing agent is a triblock copolymer, for example one chosen from the group cetyltrimethylammonium bromide (CTAB), Pluronic F-127, and Pluronic P-123. The precursor solution is then reacted with the triblock copolymer solution, by addition of a sufficient amount of the latter, dropwise, to the inorganic precursor

solution at an appropriate temperature which, in some embodiments, is 40° C. The resulting solution is stirred for a sufficient amount of time (e.g., 30 minutes in some embodiments). The resulting homogenous gel is transferred to an autoclave and heated at about 180° C under autogeneous pressure in a static condition for about 20 hours.

[00016] The resulting solid catalytic material is separated, washed at least once with water, and dried overnight at 100° C, then calcined in air at about 350° C for a sufficient amount of time, for example 5 - 10 hours. A solid catalyst prepared in this way takes the form of spheres with a particle size distribution typically ranging from about 0.3 mm - 2 mm. Generally, the nitrogen adsorption-desorption isotherms of the solid catalysts display type-IV adsorption isotherms, typical of mesoporous material. The solid catalysts prepared in this way display a range of mesophases indicative of the semi-crystalline nature of the material.

[00017] Surface area of a solid catalyst that was prepared ranged up to 366 m^2/g, with unimodal average pore size of about 3 nanometers (nm) – 7 nm. By comparison, surface area of mesoporous niobium oxide is generally about 200 m^2/g. Generally, the niobium content of the mixed oxide was inversely proportional to pore size, yet proportional to the size of the spheres and surface area.

[00018] Based on X-ray diffraction pattern studies, average size of the crystallites for the mixed oxides prepared in this way was relatively small, i.e., about 3 nm – 5 nm. Likewise, average size of the crystallites for niobium oxide was approximately the same. By comparison, average size of the crystallites for gallium oxide was about 14 nm. Based on high resolution transmission electron micrographs, the mixed gallium-niobium oxides displayed similar particle size (about 3 nm – 4 nm) as niobium oxide. The gallium-niobium oxides as well as pure niobium oxide (Nb_2O_5) alike displayed broad and diffusive electron diffraction ring spacing. For the mixed oxides, the rings corresponded to "d" spacings of

0.39 nm, 0.199 nm, and 0.169 nm, respectively, which correspond to "d"-spacings of (001), (002), and (182) planes in pure niobium oxide.

[00019] According to present embodiments, linear, olefinic hydrocarbons are passed over a gallium-niobium mixed oxide catalyst in a reactor or a reaction zone according to process steps and conditions as specified herein. In some embodiments, the normal, linear olefinic hydrocarbons contain at least 4 carbon atoms. In some embodiments, the reaction is carried out at temperatures in the range of about 150° - 450° C, preferably 200 - 400 ° C, and a pressure of about 1 bar – 60 bar. In some embodiments, the reaction is carried out in a batch reactor. Alternatively, the reaction is carried out in a semi-batch reactor, or a continuous flow reactor. In some embodiments, the starting materials are reacted while in a liquid state, or, alternatively, in a gaseous state. At the conclusion of the reaction, the branched olefinic hydrocarbon products are separated from the effluents within the reactor.

[00020] In connection with the example described herein, gallium-niobium oxide catalysts were prepared, as were gallium oxide and niobium oxide catalysts, as summarized in Table 1 below. The catalysts were prepared by reacting solutions of gallium and niobium precursors in alcohol with Pluronic F-127. For the inorganic precursor, mole ratios of precursor : SDA : ethanol were 1:6.1 x 10^{-3} : 350 x 10^{-3} : 9. The synthesis mole ratios of gallium to niobium prior to completing synthesis ranged from 0.2:1 to 6.6:1. Induced Coupled Plasma (i.e., ICP) is also used to determine molar composition. The ICP-determined mole ratio of gallium to nobium may differ from the synthesis mole ratio to the extent some gallium remains in solution rather than being incorporated in the catalyst. In some embodiments, the ICP-determined mole ratio of gallium to niobium is between about 0.03:1 and 2.8:1.

[00021] During synthesis, an alcoholic solution of the structure directing agent was added dropwise to the solution of gallium and niobium precursors in ethanol, at 40° C. The resultant solution was stirred for approximately 30 minutes. The resulting homogeneous gel

was then transferred to a 45 ml Teflon-lined autoclave (Parr Instruments, Inc.) and heated under autogeneous pressure in a static condition in a conventional oven at 180° C for approximately 20 hours. The white, solid catalytic material was separated by centrifuge, washed twice with water, and dried overnight at approximately 120° C, then calcined in air at 350° C for 10 hours. Surface area of the mixed gallium-niobium oxide catalysts was determined to be within a range of about 210 m^2/g – 366 m^2/g. Average pore size of the mixed oxide catalysts ranged from about 3.5 nm – 6.0 nm. Average pore volume of the mixed gallium-niobium oxides ranged from about 0.23 ml/g – 0.42 ml/g.

Table 1. Composition and physiochemical properties of prepared mesoporous Ga-Nb oxide catalysts for isomerisation of linear olefinc hydrocarbons.

Sample ID	ICP composition (Ga/Nb molar ratio)	Surface area (BET)	Average pore size (nm)	Average pore volume (cm^3/g)	Average particle size (μm)
Ga_2O_3 (comparable)	-	175	7.3	0.32	0.3
(A) $GaNb_1$	2.80	210	6.1	0.38	0.5
(B) $GaNb_2$	0.84	366	4.4	0.42	0.8
(C) $GaNb_3$	0.14	270	4.1	0.33	0.8
(D) $GaNb_4$	0.08	231	3.7	0.25	1.0
(E) $GaNb_5$	0.03	242	3.4	0.23	1.3
Nb_2O_5 (comparable)	-	196	3.2	0.17	1.8

Example 1

Catalytic isomerisation of Linear, Olefinic Hydrocarbons

[00022] Catalyst D was prepared as described above, then dried in a flow of nitrogen at 200° C for 5 hours. The dried catalyst was loaded in a high pressure autoclave reactor (Parr Instruments, Inc.). A feedstock of normal hexadecene, a linear olefinic hydrocarbon with 16 carbon atoms, was contacted, under stirring, with the catalyst at a temperature of 250° C and

hydrogen pressure of 20 bar for 3 hours. After an additional 2 hours, the reactor was cooled to room temperature, and the catalyst was separated from the reaction products by filtration. The identity of the hydrocarbon products was determined by gas chromatography using a Hewlett Packard 4890 gas chromatograph. The hydrocarbon layer contained penta-, hexa-, hepta-, and octa-decenes. The conversion of hexadecene was 78.3%. Conversion products included branched olefinic hydrocarbons with 16 carbon atoms (63.3%) as well as branched olefinic hydrocarbons with less than 16 carbon atoms (27.0%).

[00023] The iodine number of the hexadecene feedstock was 109.1. The iodine number of the conversion products as a whole was 145.8. This indicates that the number of double bonds in some of the conversion products exceeded the number of double bonds in the feedstock, indicating that some diolefins are also present in the products. Accordingly, besides the conversion of linear hexadecene to branched iso-decenes, this mixed gallium-niobium oxide catalyst also dehydrogenated some of the monounsaturated olefins to diolefins.

[00024] The above example is non-limiting and merely characteristic of multiple alternative embodiments taught and described herein. Further, it is to be understood that the embodiments described herein are not limited in their application to the details of the teachings, descriptions, and examples set forth herein. Rather, it will be understood that a process for catalytic isomerisation of linear, olefinic hydrocarbons, as taught and described according to multiple embodiments disclosed herein, is capable of other embodiments and of being practiced or of being carried out in various ways by persons having ordinary skill in the art.

[00025] Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use herein of "including," "comprising," "e.g.," such as," "for example," "containing," or "having" and

variations of these words and phrases is meant in a non-limiting way to encompass the items listed thereafter, and equivalents of those, as well as additional items.

[00026] Accordingly, the foregoing descriptions are meant to illustrate a number of embodiments and alternatives, rather than to serve as limits on the scope of what has been disclosed herein. The descriptions herein are not intended to be exhaustive, nor are they meant to limit the understanding of the embodiments to the precise forms disclosed

CLAIMS

We claim:

1. A process for catalytic isomerisation of linear, olefinic hydrocarbons, comprising the steps of:

   contacting linear olefinic hydrocarbon reactants with a catalyst; and

   isolating branched olefinic hydrocarbon products,

   wherein the catalyst is a solid gallium-niobium mixed oxide catalyst having a synthesis mole ratio of gallium to niobium between about 0.2:1 and 6.6:1 and a surface area of at least 210 m^2/g.

2. The process of claim 1, wherein the surface area of the catalyst is between about 300 m^2/g and 366 m^2/g.

3. The process of claim 1, wherein the ICP-determined mole ratio of gallium to niobium is between about 0.03:1 and 2.8:1.

4. The process of claim 1, carried out at a temperature between about 150 ° C and about 450 ° C.

5. The process of claim 4, carried out at a temperature no greater than about 400 ° C.

6. The process of claim 1, wherein each linear olefinic hydrocarbon reactant has no more than 35 carbons.

7. The process of claim 6, wherein each linear hydrocarbon reactant has between 4 and 19 carbons.

8. The process of claim 1, wherein the catalyst is prepared by adding a solution of at least one structure directing agent in alcohol to a solution of gallium and niobium in alcohol under conditions and for a duration sufficient to react a sufficient amount of the reactants to form a mixed gallium-niobium oxide catalyst having a synthesis mole ratio of gallium to niobium between about 0.2:1 and 6.6:1.

9. The process of claim 8, wherein the structure directing agent is chosen from the group cetyltrimethylammonium bromide, Pluronic F-127, and Pluronic P-123.

10. A branched olefinic hydrocarbon, produced by:

contacting linear olefinic hydrocarbon reactants with a catalyst; and

isolating branched olefinic hydrocarbon products,

wherein the catalyst is a solid gallium-niobium mixed oxide catalyst having a synthesis mole ratio of gallium to niobium between about 0.2 : 1 and 6.6 : 1 and a surface area of at least 210 m^2/g.

11. The hydrocarbon of claim 10, wherein the surface area of the catalyst is between about 300 m^2/g and 366 m^2/g.

12. The hydrocarbon of claim 10, wherein the synthesis mole ratio of gallium to niobium is between about 0.2:1 and 6.6:1.

13. The hydrocarbon of claim 10, wherein the linear olefinic hydrocarbon reactants are derived from triglyceride esters in a feedstock, wherein the feedstock is chosen from the group plant oils, animal fats, animal oils, and algae oils.

14. The hydrocarbon of claim 10, carried out at a temperature between about 150 ° C and about 450 ° C.

15. The hydrocarbon of claim 14, carried out at a temperature no greater than about 400 ° C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/31622

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01J 23/04, B01J 23/20 (2012.01)
USPC - 585/646; 502/306
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 585/646; 502/306

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST(USPT,PGPB,EPAB,JPAB); Google Web; Google Patents
Search Terms: catalytic, isomerization, olefin, branched, gallium, niobium, ratio, oxide, temperature, surface area, oil, tiglyceride ester

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/0056839 A1 (Ramachandran et al.) 04 March 2010 (04.03.2010) para [0029]; [0043]; [0047]-[0048]; [0059]; [0063]	1-15
Y	US 2002/0045787 A1 (Le Peltier et al.) 18 April 2002 (18.04.2002) para [0015]; [0019]; [0026]	1-15
Y	US 2008/0229654 A1 (Bradin) 25 September 2008 (25.09.2008)para [0008]-[0009]; [0012]; [0138]	1-15
Y	US 2011/0039102 A1 (Chaumonnot et al.) 17 February 2011 (17.02.2011)para [0020]; [0029]	8-9
Y	US 2003/0191330 A1 (Zhang et al.) 09 October 2003 (09.10.2003) entire document	1-15

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 June 2012 (20.06.2012)	13 JUL 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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