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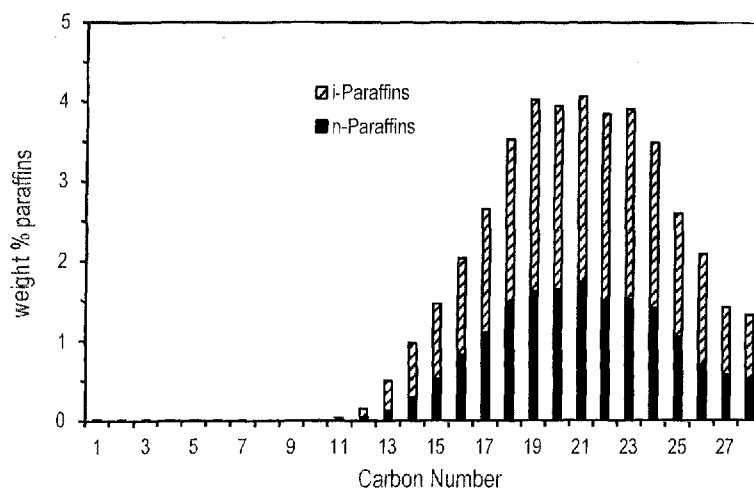


FIG. 1

(57) Abstract: Provided is a stable and efficient process for hydro-normalizing a stream comprising n-paraffins. The reaction is run in the presence of an LTA type zeolite, which zeolite has an acid site concentration preferably about 2.7 mol/l or greater. A boiling range of n-paraffins is then collected from the hydroprocessing reactor comprising C₂-C₆ n-paraffins. The collected C₂-C₆ n-paraffins can then be further converted.



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STABLE PROCESS FOR HYDROCONVERSION OF NORMAL PARAFFINS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/518,385, filed on 09 August 2023, the disclosure of which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Stable process for hydroconverting normal paraffins into lighter normal paraffins with minimal formation of iso-paraffins.

BACKGROUND

[0003] For a century, hydrocracking and catalytic cracking have been used to reduce the boiling point and to increase the H/C ratio of crude oils and coal-derived liquids in refineries. Inherently, these catalytic processes also increased the iso-paraffin content of the lighter fractions. This was desirable when the intended use of the cracking products was an internal combustion engine. However, crude oil is now increasingly used for chemical manufacture, and high iso-paraffin content has become an undesirable side effect of acid-catalyzed (hydro)cracking.

[0004] Nobel Laureate George Olah established that acid catalysts do not crack n-paraffins directly into n-paraffins. Instead, acids first catalyze the conversion of n-paraffins into iso-paraffins, and only then do they crack the iso-paraffins into mostly iso-paraffins. Consequently, a product slate with a high iso-paraffin content is generally considered the signature of acid-catalyzed cracking. By contrast, a product slate with a high n-paraffin content is the signature of thermal cracking (pyrolysis).

[0005] Historically, C₅^{plus} liquids rich in normal paraffins have been prepared by selectively extracting normal paraffins from mixtures, such as petroleum or refinery intermediate streams such as naphtha. This operation is relatively expensive and is limited to the content of C₉^{minus} normal paraffins in the feedstock. For example, harvesting particularly the longer, C₉^{plus} paraffins from an adsorbent, e.g., in a pressure swing adsorption process, requires an expensive and convoluted desorption step. Normal paraffins can also be produced in the Fischer Tropsch process. In principle Fischer Tropsch products are ideal steam cracker feedstocks -even if their heaviest products exhibit too high a boiling point for easy volatilization and pyrolysis. If these heavy

products are converted into lighter products by hydrocracking over conventional acidic catalysts, an iso-paraffin-rich product will be obtained, not a normal paraffin-rich product.

[0006] Selective cracking of heavy normal paraffins to lighter normal paraffins has been disclosed in the art. For example, note U.S. Patent Publication No. 2007/0032692 and US Patent Publication No. 2023/0141033.

[0007] In G. E. Langlois, R. F. Sullivan, and Clark J. Egan, "The Effect of Sulfiding a Nickel on Silica-Alumina Catalyst" Journal of Physical Chemistry, volume 70, 1966, pp. 3666-3671 the conversion of n-decane (n-C₁₀) over nickel on amorphous silica alumina with different sulfur levels preceding or during hydrocracking is described.

[0008] Through a process called hydrogenolysis or metal-catalyzed cracking, nickel without sulfiding gives C₄-C₇ products with low i/n ratios (0.08 mol/mol), but the conversion of this catalyst is very low (7.8%), and methane yields are relatively high (0.28 wt. %). In comparison a sulfided nickel catalyst on the silica alumina has high conversion (52.8), and low methane yields (0.02 wt %) but gives C₄-C₇ products with high i/n ratios (6.6). Catalysts are now described that have the combination of good activity, low i/n ratio products, and low methane make.

[0009] In F. Regalia, L.F. Liotta, A.M. Venezia, M. Boutonneta, S. Järåsaa. "Hydroconversion of n-hexadecane on Pt/silica-alumina catalysts: Effect of metal loading and support acidity on bifunctional and hydrogenolytic activity" Applied Catalysis A General, Vol.469, 2014, pp.328-339 the conversion of n-hexadecane (n-C₁₆) over amorphous silica alumina with different hydrogen concentrations and acid site concentrations during hydrocracking is described.

[0010] Through a process called hydrogenolysis or metal-catalyzed cracking, platinum gives C₃-C₁₂ products with low i/n ratios (< 0.4 mol/mol) even at high (92%) conversion. Characteristic for metal-catalyzed cracking a high methane make was directly proportional to the concentration of exposed metal atoms and inversely proportional to n-C₁₆ conversion. Catalysts are now described that have the combination of good activity, low i/n products, and low methane make.

[0011] In D.D. Hibbits, D.W. Flaherty, E. Iglesia "Effects of Chain Length on the Mechanism and Rates of Metal-Catalyzed Hydrogenolysis of n-Alkanes" Journal of Physical Chemistry C, , Vol.120, 2016, pp.8125-8138 describes the metal-catalyzed hydrogenolytic conversion of n-paraffins, iso-paraffins and cyclo-paraffins. Catalysts are

now described that convert exclusively n-paraffins and have the combination of good activity, good stability, low i/n products, and low methane make.

[0012] Jule A. Rabo, "Unifying Principles in Zeolite Chemistry and Catalysis," in *Zeolites: Science and Technology*, editor F. Ramoa Ribeiro et al., NATO ACS Series Vol. 80, pages 291-316, 1984 (page 295-296) discloses the use of alkali-neutralized zeolites that are free of acidic hydroxyls for cracking hexane. This reference discloses pyrolysis, thermal cracking in the absence of added hydrogen and in the absence of acid sites and does not discuss hydroconversion (cracking in the presence of hydrogen and acid sites), and significant quantities of methane (3.1 wt %) and olefins are produced.

[0013] describes the use of a platinum on silica alumina catalyst for hydrocracking hexadecane (n-C₁₆), n-heptane and n-docosane (n-C₂₀ also known as eicosane), while producing low levels of methane. Significant amount of cycloparaffins are also produced, and the product is isomerized (as noted on page 40, 1st column), B. S. Greensfelder, H. H. Voge, and G. M. Good, "Catalytic and Thermal Cracking of Pure Hydrocarbons," *Industrial and Engineering Chemistry*, November 1949, pages 2573-2584, describes the evaluation of different classes of catalysts for conversion of cetane (n-C₁₆). Of particular note, adding an activated carbon substrate to a thermal pyrolysis reaction lowers the yield of undesirable methane, but also of desirable olefins as compared to pyrolysis in the absence of a substrate or in the presence of an inert substrate such as quartz or of an alkali-neutralized zeolite (cf. [0010]). Adding a substrate with acid sites as in a (UOP B) catalyst transitions the process from pyrolysis to catalytic cracking as is evident from the signature high iso-paraffin make of acid-catalyzed cracking in the absence of added hydrogen (also called catalytic cracking).

[0014] J.E. Schmidt, B. Smit, C.Y. Chen, D. Xie, T.L.M. Maesen, "Toward superior hydroisomerization catalysts through thermodynamic optimization" *ACS Catalysis* vol. 13, 2023, pp.6710-6720 summarizes the current n-paraffin hydrocracking mechanism and indicates that isomerization prior to cracking is the signature of a "balanced" hydrocracking catalyst.

[0015] GB 1003252 and US3257311 describe the use of LTA-type zeolite with encased platinum to selectively hydrocrack n-paraffins to the exclusion of iso-paraffins and of cycloparaffins that are also in the feed. on an LTA-type zeolite that encases a platinum (de)hydrogenation function. Encasing platinum inside the zeolite on a commercial scale is not practical for economic, health, safety, and environmental reasons. Catalysts are now described that convert exclusively n-paraffins and have the combination of good

activity, good stability, low i/n products, and low methane make that have the (de)hydrogenation function (platinum, palladium, rhenium, ruthenium or a combination thereof, or nickel combined with molybdenum or tungsten) loaded onto a binder, outside the LTA zeolite.

[0016] N.Y. Chen, W.E. Garwood “Selective hydrocracking of n-paraffins in jet fuels”, Industrial Engineering Chemistry Process Design and Development, 1978, vol. 17, No. 4, pp.513-518 refers to platinum-loaded, calcium-exchanged LTA-type zeolite as Pt/Ca-A and observes that “considerations of activity and stability” led to its rejection for further process studies to selectively hydrocracking n-paraffins (n-C₁₀ – n-C₁₆) in the jet boiling range. Catalysts are now described that convert exclusively n-paraffins that exhibit excellent stability despite having the platinum loaded outside the LTA-type zeolite.

[0017] There is an urgent need in the industry to diversify the crude oil value chain. The preparation of n-paraffins as a steam cracker feedstock has become important. Minimal formation of iso-paraffins is important. The industry would welcome a stable and efficient catalytic process for hydroconverting normal paraffins into lighter normal paraffins with minimal formation of iso-paraffins. The stability of such a process would create great efficiency and economic value by increasing carbon efficiency through minimizing the methane and pyrolysis oil make associated with steam cracking iso- instead of n-paraffins.

SUMMARY

[0018] Provided is a process for hydroconverting normal paraffins into lighter normal paraffins with minimal formation of iso-paraffins. The process comprises hydroconverting a hydrocarbon feedstock comprising normal paraffins under hydroconversion conditions. The feedstock generally comprises at least 3 wt. %, or in one embodiment, at least 5 wt. %, normal paraffins. The reaction is run in the presence of a specific type of zeolite-based catalyst, with the zeolite having a requisite topology and acid site density. The present zeolite is of a framework type with voids greater than 0.50 nm in diameter, which are accessible through apertures characterized by a longest diameter of less than 0.50 nm and a shortest diameter of more than 0.30 nm. The zeolite is an LTA-zeolite having an acid site concentration in the range of from 2.6 to 3.0 mol/l, in one embodiment of about 2.7 mol/l or greater. This acid site concentration for the LTA zeolite has been found critical for the stability of the process.

[0019] Among other factors the present process is stable and efficient in hydroconverting normal paraffins into lighter normal paraffins. It has been surprisingly found that the LTA zeolite used, with an acid site concentration around 2.7 mol/l, can reduce n-paraffins in high yield to n-paraffins in the ethane to naphtha boiling range of C₂-C₆ n-paraffins, and can do so continuously for months on end without losing its catalytic activity. The reaction is stable and does not exhibit any issues with feeds having extremely long n-paraffins, such as C₂₃⁺ in length. The C₂-C₆ n-paraffins can then be used as desired as building blocks for other chemicals.

BRIEF DESCRIPTION OF THE FIGURES OF THE DRAWING

[0020] FIG. 1 graphically depicts the composition of a C₁₂⁺ feed used.

[0021] FIG. 2 graphically depicts the results achieved from hydro-normalizing a largely n-C₁₂⁺ feed in accordance with the present process.

[0022] FIG. 3 graphically depicts a steam cracker production using a hydro-normalized stream prepared by the present process as a feed.

DETAILED DESCRIPTION

[0023] Definitions:

[0024] Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethylene and propylene. Steam cracker units are facilities in which feedstocks such as ethane, propane, butane, liquefied petroleum gas (LPG), and naphtha are thermally cracked or pyrolyzed in the presence of steam by a short residence time in a furnace at high temperature to produce lighter hydrocarbons. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil. The feed composition, the hydrocarbon-to-steam ratio, the cracking temperature and furnace residence time determine the product composition. Light hydrocarbon feeds such as ethane, LPGs, or light naphtha yield mostly lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphtha or even heavier oil fractions) feeds yield some of these same products, but also aromatic pyrolysis oils.

[0025] Olefins such as ethylene, propylene and butylene are the raw materials of polyolefins. Polyolefins are one of the key building blocks of the global economy.

Illustrating its critical roll to economic growth, steam cracking capacity tends to grow slightly ahead of global gross domestic product (GDP). Ethylene capacity in 2021 was 150,000 kiloton/annum (kta) and is growing at 6000-8000 kta of ethylene, produced in ever larger facilities. A current state-of-the-art cracker can produce 2000 kta of ethylene. At such large volumes feedstocks that make incrementally more ethylene have large financial benefits.

[0026] A “naphtha” cracker is generally limited to feedstocks in the naphtha boiling range of 32-193°C (C₄-C₁₀). An ethane cracker is generally limited to feeding ethane and some LPG. Most commercial liquid and gas steam crackers in current operation are naphtha and ethane crackers.

[0027] Hydroconversion and hydroconverting: A catalytic process which operates at pressures greater than atmospheric in the presence of hydrogen and which converts normal paraffins into lighter normal paraffins with a minimum of isomerization and without excessive formation of methane and ethane. This can also be referred to as hydro-normalization. Hydrotreating and hydrocracking are distinctly different catalytic processes but which also operate at pressures greater than atmospheric in the presence of hydrogen. Hydrocracking converts normal paraffins into lighter products comprising significant amounts of iso-paraffins. Hydrotreating does not convert significant quantities of the feedstock to lighter products but does remove impurities such as sulfur- and nitrogen-containing compounds. Also in comparative contrast, thermal cracking converts normal paraffins into lighter products with a minimum of branching, but this process does not use a catalyst, typically operates at much higher temperatures, forms more methane, and makes a mixture of olefins and normal paraffins.

[0028] A LTA (Linde Type A) zeolite is a zeolite that has voids greater than 0.50 in diameter, and apertures characterized by a longest diameter of less than 0.5 nm and a shortest diameter of more than 0.30 nm. Such LTA zeolites are described in the Atlas of Zeolite Structure Types, Fourth Revised Edition 1996. LTA: Type Material (iza-structure.org) suggests an aperture with a diameter of 0.41 nm.

[0029] An “aperture” in a zeolite is the narrowest passage through which an absorbing or desorbing molecule needs to pass to get into the zeolite’s interior. The diameter of the aperture, d_{app} (nm), is defined as the average of the shortest, d_{short} (nm), and the longest, d_{long} (nm) axis provided in the IZA (International Zeolite Association) Zeolite Atlas (<http://www.iza-structure.org/databases/>). Both normal- and iso-paraffins with a methyl

group can pass through apertures with a $d_{\text{long}} \geq 0.50$ nm, but only normal-paraffins can pass through apertures with $d_{\text{long}} < 0.50$ nm provided $d_{\text{short}} > 0.30$ nm.

[0030] Apertures provide access to “voids”, the wider parts in the zeolite topology. The diameter of the void, d_{void} (nm), is characterized by the maximum diameter of a sphere that one can inflate inside such a void as per the IZA Zeolite Atlas (<http://www.iza-structure.org/databases/>). This characterizes, e.g., a fairly spherical LTA void (or cage) as one with a diameter of 1.1 nm, and an elongated AFX-type void as one with a spherical diameter of 0.78 nm. Voids are defined as cages if $d_{\text{void}}/d_{\text{app}} \geq 1.4$ nm/nm. An LTA zeolite exhibits a topology with a defined combination of apertures and voids.

[0031] The present process involves the hydro-normalization of a stream comprising n-paraffins by hydroconverting normal paraffins into lighter normal paraffins with minimal formation of iso-paraffins. The process comprises hydroconverting a hydrocarbon feedstock comprising normal paraffins under hydroconversion conditions, in the presence of an LTA zeolite catalyst. The zeolite has voids greater than 0.50 in diameter, accessible through apertures characterized by a longest diameter of less than 0.50 nm and a shortest diameter of more than 0.30 nm. Most important, the present LTA zeolite exhibits an acid site concentration in the range of 2.6 to 3.0 mol/l, in one embodiment from 2.6 to 2.8 mol/l, and most preferably about 2.7 mol/l. The present zeolite can be bound with alumina and extruded into a pellet or extrudate. The extrudate is loaded with 0.1 to 0.5 wt. % Pd, although any pellet or bound zeolite can be loaded with any hydrogenation function metal.

[0032] It is the zeolite-containing base into which the metal is loaded that is critical to the present processes. For it has been found that the present catalyst comprising a LTA zeolite in accordance herewith can provide the high conversion and minimal formation of iso-paraffins. It has been found that the key features of the catalyst zeolite include access to a pore system through apertures of a size less than 0.45 nm, and with the pore system containing voids greater than 0.50 nm in diameter. In another embodiment, the zeolite has voids greater than 0.50 nm in diameter, which are accessible through apertures characterized by a longest diameter of less than 0.5 nm and a shortest diameter of more than 0.30 nm. The present LTA zeolite has such a zeolite framework. The present LTA zeolite must also exhibit an acid site concentration of from 2.6 to 3.0 mol/l, in one embodiment from 2.6 to 2.8 mol/l, and preferably about 2.7 mol/l. This is an LTA zeolite

with a higher alumina concentration than normal. Surprisingly, it provides a stable process that can run for months without interruption.

[0033] Linde Type A, framework code LTA, is one of the most used zeolites in separations, adsorption, and ion exchange. This structure contains large spherical cages (diameter ~ 11.4 Å) that are connected in three dimensions by small 8-membered ring (8MR) apertures with a diameter of 4.1 Å. LTA is normally synthesized in hydroxide media in the presence of sodium with Si/Al ~ 1 mol/mol. By changing the cation, the limiting diameter of the 8MR apertures can be tuned, creating the highly used series of adsorbents 3A (potassium form, 2.9 Å diameter), 4A (sodium form, 3.8 Å diameter) and 5A (calcium form, 4.4 Å diameter) that are used to selectively remove species such as water, NH_3 , SO_2 , CO_2 , H_2S , C_2H_4 , C_2H_6 , C_3H_6 and other n-paraffins from gases and liquids. Detergents deploy zeolite 4A because it softens water by replacing calcium and magnesium ions in “hard” water with sodium ions. While LTA zeolites are used in vast quantities for the aforementioned applications, the industry has considered the low framework Si/Al ratio and subsequent poor hydrothermal stability limits as limiting factors to succeeding under more demanding process conditions that are commonly found in catalytic applications. Yet surprisingly, the present process is found to be extremely stable and efficient using an LTA zeolite with the requisite acid site concentration of from 2.6 to 3.0 mol/l.

[0034] The stability of the present LTA zeolites with 0.4 nm wide constrictions in hydroconverting n-alkanes, especially n-alkanes, longer than n-hexane (n-C_6) is stunning. The discovered stability of the present LTA zeolites with 0.4 nm wide constrictions that hydrocrack n-C_{12}^+ and longer n-alkanes out of feed stocks in the vacuum gasoil boiling range for at least three months is not intuitive. It is not intuitive because n-C_{12}^+ and longer n-alkanes inherently hydrocrack into branched alkanes. This would imply that the primary branched alkene and alkane products would have further isomerized into n-alkenes so as to egress through 0.4 nm wide constrictors. Particularly for i-butanes (that are allegedly primary cracking products) it is not clear what mechanism would be involved to let them egress.

[0035] The discovered hydroprocessing stability of LTA zeolites with an acid concentration as high as 2.7 mol/l is truly a surprise. Previously, it has been shown that the stability is inversely proportional to acid concentration, and the longheld belief in the industry is that stable operation requires an acid concentration of at most 1.8 mol/l. At acid concentrations higher than 1.8 mol/l, catalysts are supposed to coke up or crumble.

[0036] The stable operation of the present LTA zeolite with an acid concentration as high as 2.7 mol/l (well above the historically suggested 1.8 mol/l threshold or the estimated < 0.2 mol/l acid concentration of Pt/Ca-A in [0016]) in the hydro-normalization of n-alkanes, even n-alkanes as long as $n\text{-C}_{12}^+$, remains a mystery and surprise. The present LTA zeolite having the requisite acid site concentration can continue in operation for at least 3 months and even longer, e.g., 6 months to a year. This is counter intuitive, yet this is what has been discovered. And this surprising stability provides an efficient process for producing naphtha, which reaction need not be stopped to replace or regenerate the catalyst.

[0037] The catalyst based on the present LTA zeolite can typically contain a catalytically active hydrogenation metal. The presence of a catalytically active hydrogenation metal leads to product improvement, especially IV and stability. Typical catalytically active hydrogenation metals include chromium, molybdenum, nickel, vanadium, cobalt, tungsten, zinc, platinum, and palladium. The metals platinum and palladium are especially preferred, with platinum most especially preferred. If platinum and/or palladium is used, the total amount of active hydrogenation metal is typically in the range of 0.1 wt. % to 5 wt. % of the total catalyst, usually from 0.1 wt. % to 2 wt. %.

[0038] The zeolite can be loaded with a hydrogenation function metal or a mixture of such metals either as is or bound with a suitable binder, such as silica, alumina or titania. Such hydrogenating metals are known in the art and have been discussed generally earlier. The preferred metal is typically either a noble metal, such as Pd, Pt, and Au, or a base metal, such as Ni, Mo and W. A mixture of the metals and their sulfides can be used. The loading of the zeolite with the metals can be accomplished by techniques known in the art, such as impregnation or ion exchange. The hydrogenation function metal is loaded on such a selected zeolite to create the catalyst. The created catalyst can then be used in the hydroconversion process.

[0039] The feedstock for the process is a hydrocarbon feedstock which comprises at least 5 wt. % normal paraffins. Greater benefit is achieved when the hydrocarbon feedstock comprises at least 20 wt. %, even better when at least 50 wt. % normal paraffins, and in particular at least 80 wt. % normal paraffins. Such feedstocks can be obtained from a wide variety of sources. Typical heavy feedstocks can include hydrotreated or hydrocracked gas oils, biogenic animal fats, vegetable oils, or greases (FOG). Other hydrocarbon feedstocks suitable for use in the present process scheme may be selected, for example, from gas oils, vacuum gas oils, oils derived from waste plastics, sorted

municipal waste, end-of-life tires or biomass through pyrolysis or through hydrothermal liquefaction; residuum fractions from an atmospheric pressure distillation process; solvent-deasphalted petroleum residua; shale oils, and cycle oils. Biogenic oils and so-called circular oils (i.e., oils made from waste materials). Vacuum gas oils is a preferred feedstock for the first step of the present process.

[0040] In an embodiment, the feedstock's aromatics and organic nitrogen, sulfur, oxygen, halogen and silicon content is reduced. This can be achieved by hydrotreating the feedstock prior to the hydroconversion. Contacting the feedstock with a hydrotreating catalyst may serve to effectively hydrogenate aromatics in the feedstock and to remove N-, S-, O-, Cl-, Br-, F-, Si- containing compounds from the feed.

[0041] The conditions under which the hydro-normalization reaction or hydroconversion reaction is carried out will generally include a temperature within a range from about 390° F to about 800° F (199° C to 427° C). In an embodiment, the temperature is in the range from about 550° F to about 700° F (288° C to 371° C). In a further embodiment, the temperature may be in the range from about 590° F to about 675° F (310° C to 357° C). The pressure may be in the range from about 50 to about 5000 psig, and typically in the range from about 100 to about 2000 psig.

[0042] The normal paraffin-rich product recovered from the hydroconversion can then be used as desired. For example, as a solvent in the paint industry, as a raw material in making chemicals, for further processing into fuels or even gasoline. One important use would be as a feed to a steam cracker.

[0043] Using the present LTA zeolite-based catalyst with the higher acid site concentration provides a C₂-C₆ product in improved yields, which product can be collected from the hydroconversion process. The product can then be passed to a steam cracker. The steam cracking process is known in the art. Steam cracking a hydrocarbon feedstock produces olefin streams containing olefins such as ethylene, propylene, and butenes as well as aromatics. The present hydroconversion process provides an excellent feedstock for a steam cracker because it increases the ethylene yield at the cost of propylene and aromatics yields. As well, its stability renders the overall process incredibly efficient and economic.

[0044] In steam cracking, a gaseous or liquid hydrocarbon feed like ethane, LPG, light or full-range naphtha is diluted with steam and heated in a furnace in the absence of oxygen. Typically, the reaction temperature is between 800 and 900°C and the residence time is on the order of milliseconds. The pyrolyzing gases flow at close to the speed of sound.

After pyrolysis, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil.

[0045] The products produced in the reaction depend on the composition of the feed and on the conditions, such as the hydrocarbon-to-steam ratio, the cracking temperature and furnace residence time. Light hydrocarbon feeds (ethane, LPG, light naphtha) yield lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon feeds (full range and heavy naphtha, hydrogenated gas oils) also yield these lighter products as well as aromatic pyrolysis oils suitable for aromatics extraction and for use in the production of needle coke or synthetic graphite. The present process is directed to preparing lower alkenes, and in particular ethylene and at minimizing pyrolysis oil make. The C₂-C₆ light naphtha range prepared by the LTA zeolite hydroconversion allows for high yields of lower alkenes such as ethylene.

[0046] The following examples are provided in order to further illustrate the present process. However, the examples are not meant to be limiting.

Example 1

[0047] Example of LTA zeolite based noble metal catalyst.

[0048] A catalyst was made by extruding 50 wt. % LTA zeolite with 50- wt-% alumina (Pural TH80 from Sasol). The KAQ-type extrudates were loaded with 0.5 wt. % Pd. The LTA zeolite used had an acid site concentration of about 2.7 mol/l.

Example 2

[0049] A process to selectively hydro-normalize the long n-paraffins in a feedstock into particularly C₂-C₆ n-paraffins has been discovered. The process thereby provides a tailored feedstock for a naphtha steam cracker, which selectively pyrolyzes the C₂-C₆ n-paraffins to monetize these hydro-normalized products.

[0050] Hydro-normalization is accomplished through hydroprocessing an industrial feedstock (e.g., a 1st stage hydrocracker effluent in the vacuum gasoil boiling range at 1550 psia H₂, 1.6 LHSV, 5100 scf/b H₂,) on a hydroprocessing catalyst as described in Example 1, comprising a LTA zeolite with an optimum acid site concentration around 2.7 mol/l. Key features of the hydro-normalization process are that the catalyst selectively converts longer normal paraffins in the feed into C₂-C₆ n-paraffins. Since the feed in the example has an initial boiling point of 390 F, the shortest n-paraffin in feed is

n-dodecane (or n-C₁₂ with a 421 F boiling point, whereas n-undecane or n-C₁₁ exhibits a 385 F boiling point).

[0051] See FIG. 1 which shows a feed exclusively containing n-C₁₂^{plus} with negligible n-C₁₂^{minus}. The products at 81% n-C₁₂^{plus} conversion are nearly exclusively C₂-C₅ n-paraffins. See FIG. 2.

[0052] Contrary to the expectations of the art, the present LTA zeolites have been surprisingly found to not exhibit a dramatic preference for processing n-paraffins up to the length that could easily fit inside a single LTA cage, which would limit the length of readily hydrocracked n-paraffins to that of n-tricosane or n-C₂₃ (716°F boiling point) Longer n-paraffins (n-triacontane or n-C₃₀, 840°F boiling point and longer) are still successfully processed. In addition to a remarkable selectivity for hydrocracking selectively n-C₁₂ and longer n-paraffins into n-paraffins, the catalyst also makes minimal i-paraffins.

Example 3

[0053] Example of steam cracker feed properties.

[0054] A hydrotreated vacuum gasoil is hydroprocessed into an improved steam cracker feed as described in Table 1 below at 1550 psia H₂, 1.6 LHSV, 5100 scf/b H₂. A steam cracker feed produced at 60% n-C₁₂⁺ conversion in the present hydro-normalization step is characterized in Table 1 as follows:

TABLE 1

	Feed	Hydroprocessed
API (°)	35.4	not measured
S (ppm-wt)	5.3	<0.3
N (ppm-wt)	<0.3	<0.3
wt-% paraffins (GCxGC)	45	52
wt-% n-C ₁₂ ⁺	18	0
wt-% C ₂ - n-C ₆	0	12
Composition	Wt%	Wt%
Methane	0.00	0.03

Ethane	0.00	0.04
Propane	0.00	1
i-Butane	0.00	0.2
n-Butane	0.00	1.29
C4-	0.00	2.56
C5-180°F	0.00	2.2
180-350°F	0.00	0.59
350-500°F	7.2	9.58
500°F+	92.8	86.13
C5+	100.0	98.5
WLP Dist, by Wt%		
0.5/5%	392/478	95/445
10/30%	519/606	495/598
50%	666/	660/
70/90%	719/799	716/796
95/99.5%	842/955	840/956

[0055] The distribution between n- and iso-paraffins as determined by GC x GC is as shown in FIG. 3.

[0056] When switching from a feed without hydro-normalization to one with hydro-normalization, a dramatically lower feed rate (ton/hr) is needed to reach the same desirable ethylene (C₂H₄) yield. At this feed rate, the hydronormalized feed exhibits a shift toward desirable olefins (C₂H₄, C₃H₆, C₄H₈) and aromatics (benzene, toluene, xylenes or BTX) at the cost of heavier products (particularly pyrolysis fuel oil or PFO) (see Table 2 below). This amounts to a dramatic increase in carbon and energy efficiency of the steam cracking process.

TABLE 2

	Original Feed		Hydroprocessed	
	High Sev	Low Sev	High Sev	Low Sev
Feed, T/h	324.1	392.7	307.7	379.1
H₂	2.4	2.2	2.4	2.1
CH₄	37.2	34.2	37.1	33.6
C₂H₄	100	100	100	100
C₃H₆	46.1	62.2	41.9	61.3
C₄H₆	18.2	21.9	17.8	21.7
C₄H₈	11.4	24	9.8	23.8
C₄H₁₀	0.4	0.6	0.4	0.6
C5-400F PGO	61.4	77.2	58.1	76.3
400F+ PFO	47	70.4	40.4	59.8
Selectivity, w/w				
C₂H₄	30.86	25.46	32.5	26.38
C₂H₄+C₃H₆	45.07	41.3	46.12	42.53
C₂H₄+C₃H₆+C₄H₈	50.69	46.87	51.9	48.27
BTX	12.08	7.44	12.6	7.45

[0057] As used in this disclosure the word “comprises” or “comprising” is intended as an open-ended transition meaning the inclusion of the named elements, but not necessarily excluding other unnamed elements. The phrase “consists essentially of” or “consisting essentially of” is intended to mean the exclusion of other elements of any essential significance to the composition. The phrase “consisting of” or “consists of” is intended as a transition meaning the exclusion of all but the recited elements except for only minor traces of impurities.

[0058] As those skilled in the art will appreciate, numerous modifications and variations of the present invention are possible considering these teachings, and all such are contemplated hereby. For example, in addition to the embodiments described herein, the present invention contemplates and claims those inventions resulting from the

combination of features of the invention cited herein and those of the cited prior art references which complement the features of the present invention. Similarly, it will be appreciated that any described material, feature, or article may be used in combination with any other material, feature, or article, and such combinations are considered within the scope of this invention.

[0059] All of the publications cited in this disclosure are incorporated by reference herein in their entireties for all purposes.

What is claimed is:

1. A process comprising subjecting a hydrocarbon feedstock comprising at least 5 wt. % normal paraffins to a hydroconversion reaction under hydroconversion conditions in the presence of a LTA-type zeolite-based catalyst, the zeolite having an acid site concentration in the range of from 2.6 to 3.0 mol/l and a crystal size in the range from 10 to 1000 nm.
2. The process of claim 1, wherein a C₂-C₆ comprising product stream is collected from the hydroconversion reaction.
3. The process of claim 1, wherein the process is run for at least two years without changing the LTA catalyst or regenerating the LTA catalyst.
4. The process of claim 1, wherein the LTA zeolite is bound with a binder, and the resulting catalyst base (bound zeolite) is loaded with a hydrogenation function metal or mixed transition metal sulfides.
5. The process of claim 4, wherein the hydrogenation function metal comprises a noble metal.
6. The process of claim 5, wherein the noble metal comprises Pd, Pt, Re, Ru, Sn, Au or a mixture thereof.
7. The process of claim 4, wherein the hydrogenation function metal component comprises Ni, Co, Mo, W, their sulfides, or a mixture thereof.
8. The process of claim 1, wherein the acid site concentration of the LTA zeolite is in the range of from 2.6 to 2.8 mol/l at 10-1000 nm crystal size.
9. The process of claim 1, wherein the acid site concentration of the LTA zeolite is about 2.7 mol/l at 10-1000 nm crystal size.

10. The process of claim 1, wherein the process is run for at least 4 years without changing the LTA zeolite-based catalyst or regenerating said LTA based catalyst.
11. The process of claim 1, wherein the feedstock is a vacuum gas oil based feedstock.
12. The process of claim 1, wherein the feedstock is subjected to a hydrotreatment prior to the hydroconversion reaction.
13. The process of claim 1, wherein the per-pass conversion of the normal paraffins in the feedstock is between 20 and 99%.
14. The process of claim 2, wherein the product stream is further converted to chemicals.
15. The process of claim 2, wherein the product stream is used in the preparation of fuels or gasoline.
16. The process of claim 4, wherein the binder is an alumina with a pore volume in the 11-20 nm pore diameter range of 0.2 to 1.0 cc/g.

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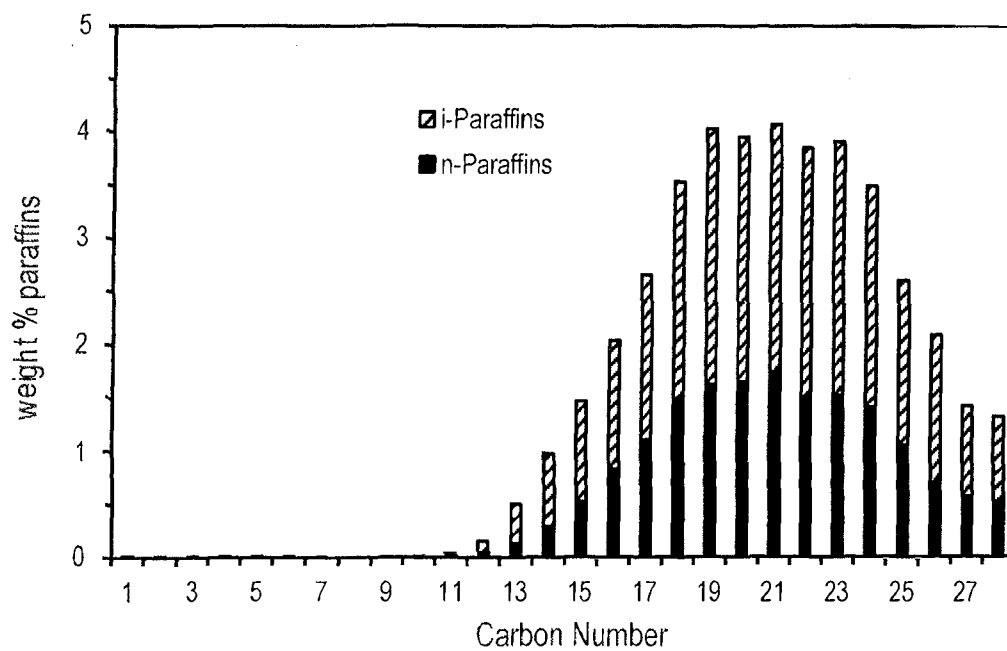


FIG. 1

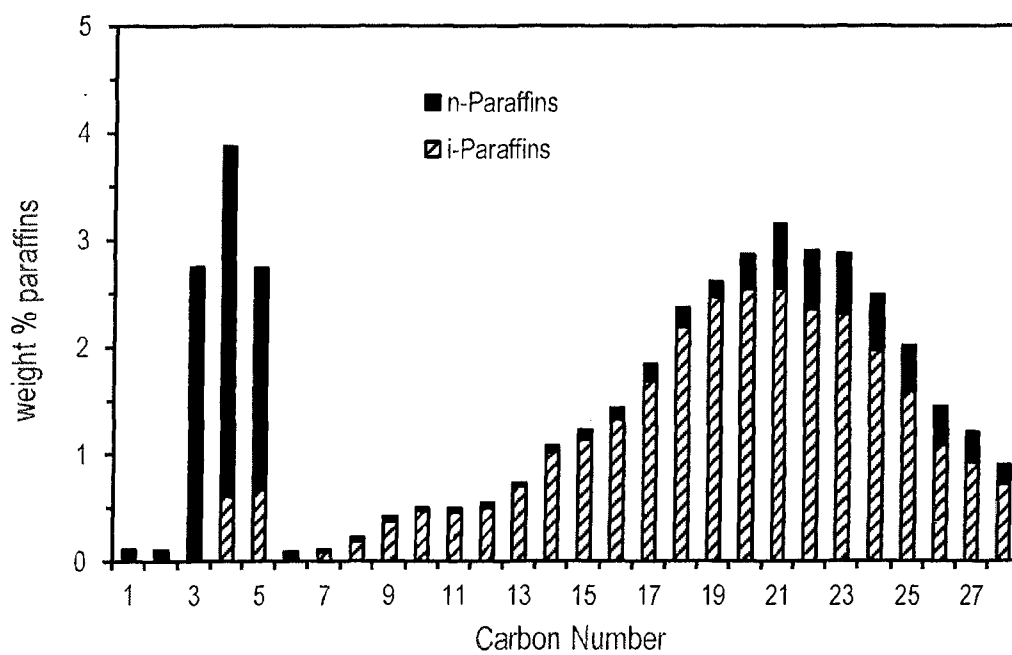


FIG. 2

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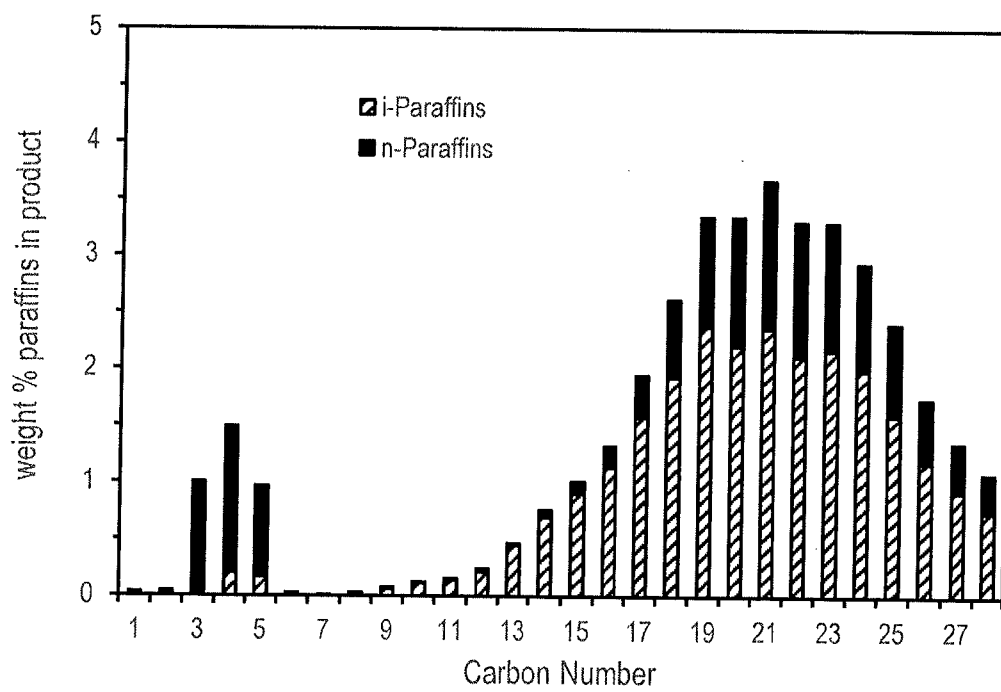


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/041735

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C10G9/36	C07C11/04	C10G11/05	B01J29/72	B01J29/74
	B01J29/76	C10G47/18	C10G47/20		
ADD.					
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)					
C10G C07C B01J					
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)					
EPO-Internal, CHEM ABS Data, COMPENDEX, WPI Data					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
X	WO 2022/144802 A1 (CHEVRON USA INC [US]) 7 July 2022 (2022-07-07) paragraph [0033] - paragraph [0038]; claims; figures paragraph [0047]; examples -----				1 - 16
A	WO 2017/180458 A1 (SAUDI ARABIAN OIL CO [SA]; ARAMCO SERVICES CO [US]) 19 October 2017 (2017-10-19) paragraph [0004] - paragraph [0013] ----- - / - -				1 - 16
☒ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
* Special categories of cited documents :					
"A" document defining the general state of the art which is not considered to be of particular relevance			"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		
"E" earlier application or patent but published on or after the international filing date			"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		
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"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search			Date of mailing of the international search report		
16 October 2024			29/10/2024		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Van der Poel, Wim		

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/041735

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BEN W. BOAL ET AL: "Facile Synthesis and Catalysis of Pure-Silica and Heteroatom LTA", CHEMISTRY OF MATERIALS, vol. 27, no. 22, 24 November 2015 (2015-11-24), pages 7774-7779, XP055381605, US ISSN: 0897-4756, DOI: 10.1021/acs.chemmater.5b03579 abstract -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/041735

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