

INCREASING OCTANE NUMBER OF LIGHT NAPHTHA USING A GERMANIUM-ZEOLITE CATALYST

SPECIFICATION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION: This invention relates to a process for the increasing the octane number of a naphtha hydrocarbon feed having a predominantly paraffin content with a base-exchanged zeolite with germanium in the crystalline framework and with a noble metal deposited on the zeolite, for example Pt/CsGeZSM-5.

DESCRIPTION OF THE PRIOR ART:

Naphtha is a mixture mainly of straight-chained, branched and cyclic aliphatic hydrocarbons, light naphtha having from five to nine carbon atoms per molecule and heavy naphtha having from seven to nine carbons per molecule. Typically, light naphtha contains naphthenes, such as cyclohexane and methylcyclopentane, and linear and branched paraffins, such as hexane and pentane. Light naphtha typically contains 60% to 99 % by weight of paraffins and cycloparaffins. Light naphtha can be characterized as a petroleum distillate having a molecular weight range of 70-150 g/mol, a specific gravity range of 0.6-0.9 g/cm³, a boiling point range of 50-320°F and a vapor pressure of 5 to 500 mm Hg (torr) at room temperature. Light naphtha may be obtained from crude oil, natural gas condensate or other hydrocarbons streams by a variety of processes, e.g., distillation.

The octane number of a liquid hydrocarbon is the measure of the ignition quality when burnt in a standard (spark-ignition internal combustion) engine. The higher this number, the less susceptible is the hydrocarbon to 'knocking' (explosion caused by its premature burning in the combustion chamber). The octane number represents a mixture of isooctane and n-heptane having the same antiknock properties as the fuel, i.e., a hydrocarbon having an octane number of 92 has the same knock as a mixture of 92% isooctane and 8% n-heptane. The octane number is often determined by means of a standardized test, such as ASTM 2699 or ASTM 2700. Generally, the octane number is increased by decreasing the linear paraffin content of the hydrocarbon.

One means of decreasing the linear paraffin content of the hydrocarbon is by isomerizing the paraffins from predominantly linear to predominantly branched. U.S. Patent no. 7,414,007 discloses a catalyst and process for isomerization of a paraffinic feedstock to obtain a higher octane hydrocarbon. The catalyst is a support of an oxide or hydroxide of a Group IVB metal (zirconium, titanium or hafnium) which has been tungstated by treatment with a tungsten compound to form a strong acid and on which is deposited a phosphorus compound and a platinum compound. The catalyst is used in the isomerization process to convert linear paraffins to isoparaffins.

Another means of decreasing linear paraffin content of the hydrocarbon is by preferential adsorption. U.S. Patent no. 7,037,422 discloses a process for producing a high RON (research method octane number, ASTM C2699) naphtha by contacting a hydrocarbon feed stream of a

mixture of isomers of C₅ and C₆ paraffins with a CFI zeolite, such as CIT-5, in an adsorption zone whereby the branched isomers of the C₅ and C₆ paraffins are preferentially adsorbed compared to the straight chain isomers and recovering a naphtha product from the adsorption zone. Since for a given carbon number, the shortest, most branched isomer tends to have the highest octane number, increasing the proportion of these high octane isomers in the hydrocarbon increases the octane number of the hydrocarbon overall. The CFI zeolite can also be a hydroisomerization catalyst to selectively isomerize n-C₅ and n-C₆ to branched isomers. The CFI zeolite may contain a metal such as platinum, palladium, iridium or a mixture of platinum and palladium, active for hydroisomerization. U.S. Patent no. 7,029,572 discloses a similar process using an ATC zeolite, such as SSZ-55.

Another means of decreasing paraffin content of the hydrocarbon is by aromatizing the paraffins to aromatics. U.S. Patent no. 6,083,379 discloses a process for desulfurizing and enhancing octane number by aromatizing hydrocarbons. The catalyst is a zeolite, such as ZSM-5, with an activity promoter, such as a metal or metal oxide of Groups IA, IIA, IIIA, IVA, VA, VIA, IIB, IIIB, IVB, VB, VIB or VIII.

U.S. Patent no. 6,245,219 discloses a process for reforming a naphtha-containing hydrocarbon feedstream containing at least about 25 wt% of C₅ to C₉ aliphatic and cycloaliphatic hydrocarbons with a catalyst of a ZSM-5 and a dehydrogenation metal, such as gallium, zinc, indium, iron, tin or boron, said catalyst being modified with a Group IIA alkaline earth metal, such as barium, or an organosilicon compound sufficient to neutralize 50%-90% of the surface

acidic sites. The aromatization of the n-paraffins to aromatics results in a higher octane rating of the resulting product.

U.S. Patent no. 6,177,374 discloses a catalyst of oxides of silicon, zinc and aluminum used for the production of high octane aromatics, such as benzene, toluene, xylenes, from natural gas condensate (NGC) and light naphtha. The catalyst is represented as $M_{2/n}O$, $x Al_2O_3$, $y SiO_2$, $z ZnO$, where M is a proton and/or a metallic cation, n is the valency of the cation and x, y and z is the number of moles of Al_2O_3 , SiO_2 and ZnO and y/x (SiO_2/ZnO molar ratio) is a number ranging from 5 to 1000.

U.S. Patent no. 5,510,016 discloses a process for catalytically desulfurizing cracked fractions in gasoline with a hydrotreating step which reduces octane number followed by treatment with self-bound or binder-free zeolite to restore lost octane. Light naphtha generally does not contribute higher octane values without reforming. Catalytic reforming can increase octane number by converting a portion of paraffins and cycloparaffins to aromatics but a platinum type reforming catalyst is generally not sulfur tolerant. Desulfurization with hydrotreating lowers the octane number of the feed which is restored by converting low octane number paraffins to higher octane number products, e.g., selective cracking of heavy paraffins to lighter paraffins, cracking of low octane paraffins, generation of olefins, ring opening to yield high octane components and dehydrocyclization and aromatization of paraffins to alkylbenzenes.

It would be advantageous to have a sulfur-tolerant catalyst for increasing the octane number of a naphtha hydrocarbon feed having a predominantly paraffin content.

SUMMARY OF THE INVENTION

5 The octane number of a naphtha hydrocarbon feed with a predominantly paraffin content is increased by contacting the hydrocarbon feed with a catalyst which comprises a non-acidic germanium zeolite on which a noble metal, such as platinum, has been deposited. The zeolite is non-acidic. Examples of the zeolite structure are MTW, FER, MEL, TON, MRE, MWW, MFI, BEA, MOR, LTL or MTT. In one embodiment of the invention the zeolite has a MFI structure.

10 The term "ZSM-5" is used in this Specification to mean a zeolite having a MFI structure. The zeolite has silicon, germanium and, optionally, aluminum in the crystalline framework of the zeolite structure. One example of the catalyst is an aluminosilicate zeolite having germanium in the framework which has been base-exchanged such that it is nonacidic and on which platinum has been deposited, e.g., Pt/CsGeZSM-5. This catalyst is sulfur tolerant up to a level of 1000 ppm in

15 the hydrocarbon feed.

 The process for increasing octane number of a hydrocarbon feed comprising: a) contacting at conditions for concurrently isomerizing n-paraffins to isoparaffins, further isomerizing isoparaffins to more highly branched isoparaffins, cracking n-paraffins to smaller n-isoparaffins, dehydrogenating both n- and iso- paraffins and dehydrocyclizing n-paraffins to aromatics a

20 hydrocarbon feed comprising naphtha having C₆-C₈ alkanes, with a catalyst comprising a non-acidic

medium pore or large pore zeolite comprising silicon, germanium and, optionally, aluminum on which a noble metal has been deposited; and b) recovering a hydrocarbon product. The naphtha feed may have a C₆-C₈ content of at least 30%, at least 40% or at least 50%.

DETAILED DESCRIPTION OF THE INVENTION

Zeolite is a crystalline hydrated aluminosilicate that may also contain elements other than aluminum and silicon in the crystalline framework. The term "zeolite" includes not only aluminosilicates but substances in which the aluminum is replaced by other trivalent elements, and substances in which silicon is replaced by other tetravalent elements. Generally, zeolites are structures of TO₄ tetrahedra, which form a three dimensional network by sharing oxygen atoms where T represents tetravalent elements, such as silicon, and trivalent elements, such as aluminum. Zeolites are known catalysts for isomerization, toluene disproportionation, transalkylation, hydrogenation and alkane oligomerization and aromatization. Some zeolite catalysts, especially those containing a Group VIII deposited metal, are susceptible to sulfur poisoning.

A catalyst of a germanium zeolite (Ge-zeolite) on which a noble metal has been deposited is base-exchanged with an alkali metal or alkaline earth metal to reduce acidity. The base-exchange may occur before or after the noble metal is deposited. The catalyst is used to increase the octane number of natural gas condensate, light naphtha or raffinate from aromatics extraction and other refinery or chemical processes, provided such condensate, naphtha or raffinate has a predominant

paraffin content.

The silicon to aluminum atomic ratio ($\text{Si}:\text{Al}_2$) of the zeolite is $40-\infty$. One example, without limiting the invention, is a $\text{Si}:\text{Al}_2$ atomic ratio in the range from 40 to 500. Another example, without limiting the invention, is a $\text{Si}:\text{Al}_2$ atomic ratio in the range from 50 to 150.

5 The zeolite of the present invention is a medium pore zeolite or large pore zeolite. The term “medium pore” in this Specification should be taken to mean average pore size is in the range from about 5 to about 7 angstroms. The term “large pore” in this Specification should be taken to mean average pore size is in the range from about 7 to about 10 angstroms. It is possible that these ranges could overlap and a particular zeolite might be considered either a medium pore zeolite or a large
10 pore zeolite. Zeolites having an average pore size of less than about 5 angstroms, i.e., a “small pore” zeolite, would not be considered either a medium pore zeolite or a large pore zeolite. A small pore zeolite would not allow molecular diffusion of the molecules of the desired aromatic products, e.g., benzene, ethyl benzene, toluene and xylenes, in its pores and channels. Some zeolites have two distinct channels of different sizes, e.g., MOR has a 12-ring channel that is 7.0 x 6.5 angstroms
15 as well as an 8-ring channel than is <5 angstroms. Multichannel zeolites which have at least one channel which is within the ranges above for a medium pore zeolite or a large pore zeolite are considered within the scope of zeolites useful for the present invention. Examples of medium pore zeolites and large pore zeolites, without limiting the invention, are MFI, BEA, LTL, MOR and MTT.

20 The germanium content of the zeolite is in the range from 1.0% to 10.0% by weight. One

example of germanium content of the zeolite is from 3.5% to 6.0% by weight.

The noble metal is deposited on the zeolite by any known method of depositing a metal on a zeolite. Typical methods of depositing a metal on zeolite are ion exchange and impregnation. Deposition of the noble metal results in the noble metal being present not only on the surface of the zeolite but also in the pores and channels of the zeolite. In one example of the present invention, the noble metal is present in the catalyst in the range from 0.05% to 3% by weight. In another example of the present invention, the noble metal is from 0.2% to 2% by weight. In another example, the noble metal is from 0.2 to 1.5% by weight. Examples of the noble metal are platinum, palladium, iridium, rhodium, ruthenium and combinations thereof.

The zeolite of the present invention is non-acidic. One meaning of the term "non-acidic" in this Specification should be taken to mean a zeolite which has been base-exchanged with an alkali metal or alkaline earth metal, such as cesium, potassium, sodium, rubidium, barium, calcium, magnesium, lithium and mixtures thereof, to reduce acidity. Base-exchange may take place during synthesis of the zeolite with an alkali metal or alkaline earth metal being added as a component of the reaction mixture or may take place with a crystalline zeolite before, after or simultaneous with deposition of the noble metal. The zeolite is base-exchanged to the extent that most or all of the cations associated with aluminum are alkali metal or alkaline earth metal. An example of a monovalent base:aluminum molar ratio in the zeolite after base exchange is at least about 0.9. In one embodiment of the invention, cesium is the alkali metal and is present in a molar ratio to aluminum in the range from about 1 to about 2.

Another meaning of “non-acidic” within the present invention is an aluminum-free zeolite. An aluminum-free zeolite need not be base-exchanged to be nonacidic. The aluminum-free zeolite may contain another tetravalent or trivalent element, such as titanium, iron, gallium, boron, germanium or tin. “Aluminum-free” has a meaning of having aluminum content of no more than 0.4 wt%. Within the meaning and for the purposes of the present invention, a zeolite may be “non-acidic” by exchange with a base or by having a low aluminum content.

The zeolite may contain promoters or modifiers as are known in the art. These promoters or modifiers are present in a catalytically effective amount, e.g., about 0.1 weight percent to about 1.0 weight percent. Examples of promoters or modifiers are rhenium, iridium, palladium and tin.

The catalyst may be supported on or bound with a material, such as a metal oxide; a mixed metal oxide, e.g., oxides of magnesium, aluminum, titanium, zirconium, thorium, silicon or mixtures thereof; a clay, e.g., kaolin or montmorillonite; carbon, e.g., carbon black, graphite, activated carbon, polymers or charcoal; a metal carbide or nitride, e.g., molybdenum carbide, silicon carbide or tungsten nitride; zeolites; a metal oxide hydroxide, e.g., boehmite, to change the physical properties of the catalyst.

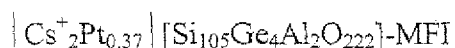
The hydrocarbon feed may contain sulfur up to 1000 ppm. In one embodiment of the invention, the hydrocarbon feed contains sulfur from about 1 ppm to about 500 ppm. In another embodiment of the invention, the hydrocarbon feed contains sulfur from about 10 ppm to about 100 ppm.

One particular example of a hydrocarbon conversion process using a zeolite catalyst is

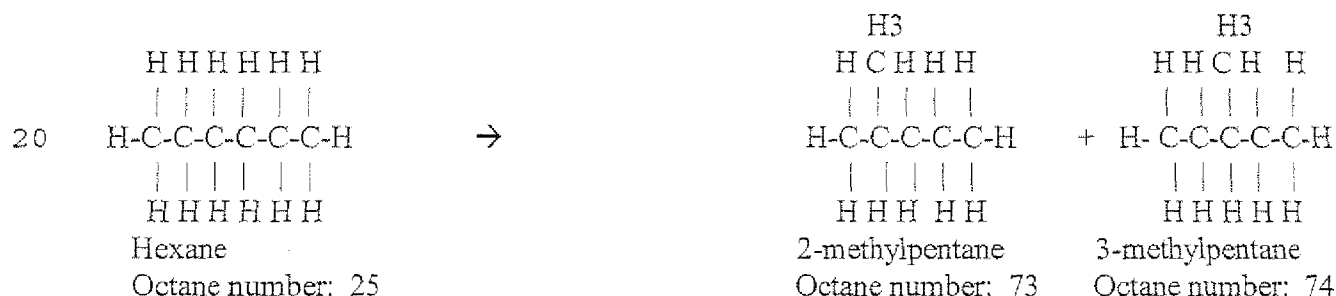
dehydrocyclization of alkanes to aromatics, e.g., C₆₊ alkanes to aromatics, primarily benzene, toluene and xylenes, as disclosed in U.S. Patent Application Publication no. 2008/0255398 published October 16, 2008, hereby incorporated by reference. The dehydrocyclization process promotes cyclization and dehydrogenates cyclics to their respective aromatics.

U.S. Patent no. 6,784,333, hereby incorporated by reference, discloses a catalyst of an aluminum-silicon germanium zeolite on which platinum has been deposited. The catalyst can be used in aromatization of alkanes, specifically, aromatization of lower alkanes, such as propane. The catalyst may be a MFI zeolite in which germanium is incorporated into the crystalline framework, i.e., Pt/Ge-ZSM-5. The catalyst may be sulfided before or during the aromatization process.

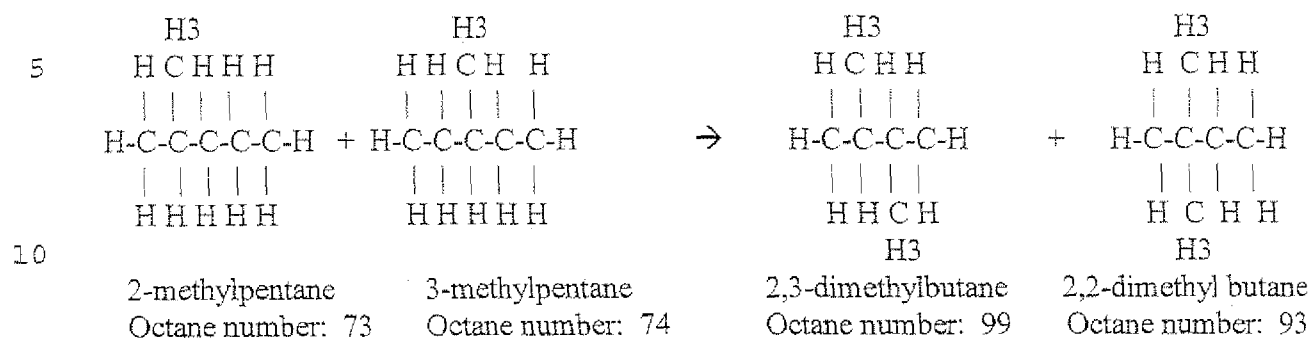
According to the IUPAC recommendations, an example of a catalyst for the present invention would be represented as:



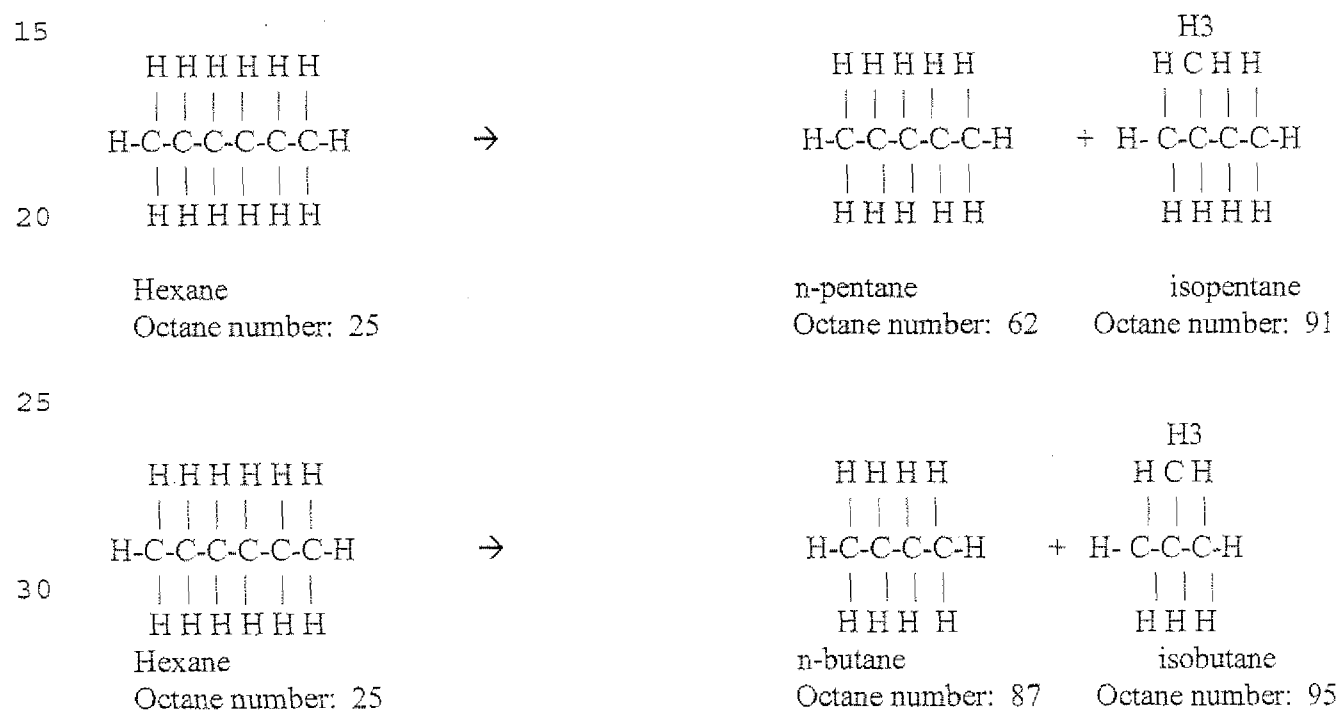
The present invention increases octane number by several reaction mechanisms which convert hydrocarbons having a relatively lower octane number to hydrocarbons having a relatively higher octane number. Nonstoichiometric examples of these reaction mechanisms are shown below. One example is isomerizing n-paraffins to isoparaffins, e.g.,



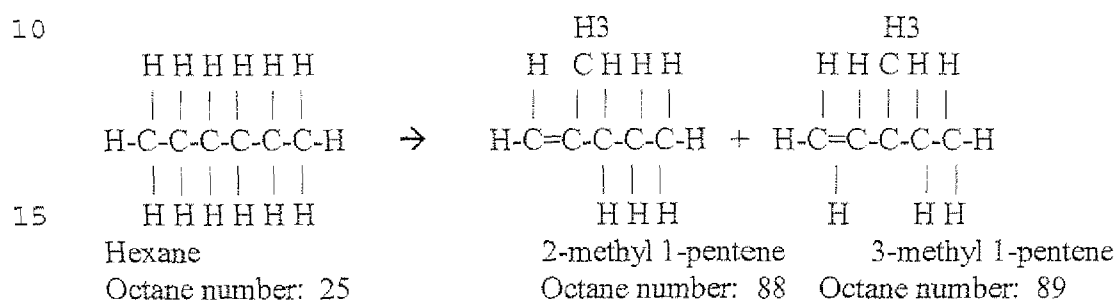
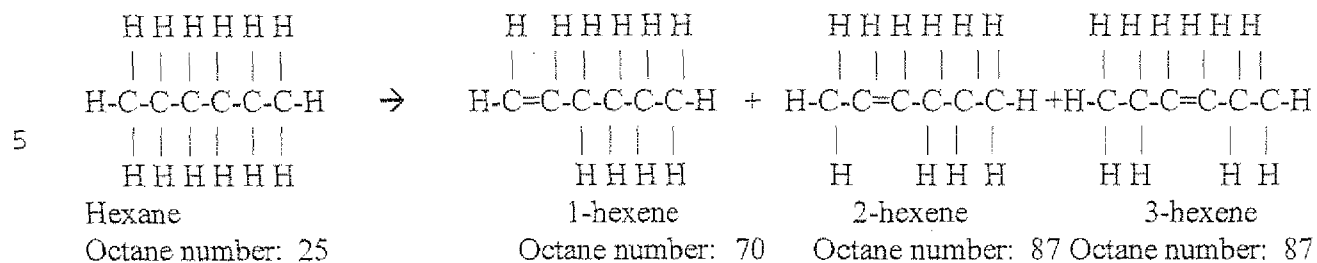
Another example is further isomerizing isoparaffins to more highly branched isoparaffins, e.g.,



Another example is cracking n-paraffins to smaller n-and iso-paraffins, e.g.,



Another example is dehydrogenating both n- and iso- paraffins, e.g.,



Another example is dehydrocyclizing n-paraffins to aromatics, e.g.,



20 It should be noted that the chemical reactions above are not chemically balanced but are presented to show reactants and products in the process of the present invention of converting hydrocarbons having a relatively lower octane number to hydrocarbons having a relatively higher octane number.

The catalyst of the present invention is capable of concurrently functioning as an isomerization, cracking, dehydrogenation and dehydrocyclization catalyst. The octane numbers for the above hydrocarbons are numerical averages of the research octane number (RON) and the motor octane number (MON) from ASTM Special Technical Publication #225, "Knocking Characteristics of Pure Hydrocarbons", i.e., $(RON + MON)/2$.

The process feed may contain hydrocarbons other than C_6 - C_8 alkanes and nonhydrocarbons, i.e., compounds which are not hydrocarbons. It may contain lower alkanes, such as pentane, and higher alkanes, such as nonane and decane. The process feed may contain isoparaffins, olefins, naphthenes and even aromatics. Those components of the feed which are not C_6 - C_8 alkanes may be hydrocarbons which catalytically react or hydrocarbons or nonhydrocarbons which are catalytically nonreactive or inert, such as diluents. In one embodiment the process feed is naphtha having at least 30% C_6 - C_8 alkanes. In another embodiment the process feed is naphtha having at least 40% C_6 - C_8 alkanes. In another embodiment the process feed is naphtha having at least 50% C_6 - C_8 alkanes.

The aromatization process may be carried out at a liquid hourly space velocity in the range between 0.1 and 100 h^{-1} , at a temperature in the range between 200 and 600°C and at a pressure in the range between 1 and 315 psia.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the

specification or the claims to follow in any manner.

CATALYST PREPARATION

The catalyst used in the examples was prepared according to the following procedure:

5 Solution #1 was made by diluting 15.84 g of 50 wt % NaOH solution with 131.25 g of deionized (DI) water and subsequently dissolving 7.11 g of germanium dioxide. Solution #2 was made by diluting 3.84 g sodium aluminate solution (23.6 wt % alumina and 19.4 wt % sodium oxide) with 153.9 g DI water. Solution #1 was added to 150 g Ludox AS-40 (40 wt % silica in a colloidal state) and vigorously stirred for 10 minutes to obtain a homogeneous mixture. Solution
10 #2 was stirred into this mixture. After 15 minutes of vigorous agitation, 105.42 g of tetra-n-propyl ammonium hydroxide (TPAOH) was added and the mixture was stirred for 60 minutes. Finally, 23.32 g of glacial acetic acid was added to the gel to adjust the pH of the mixture to about 9. This mixture was loaded into a 1 L stainless steel autoclave and heated at 160°C for 36 hours with stirring. Subsequently, the solids obtained were filtered from the mother liquor and
15 washed with DI water. The resulting solid was calcined at 550°C for 6 hours in an oven with air flow. The MFI structure of the solid was confirmed by measuring the powder X-Ray diffraction pattern.

 GeZSM-5, prepared as described above, was washed with aqueous CsNO₃ (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M CsNO₃ and rinsed with distilled
20 water on the final filtering. The zeolite powder was then calcined for 3 hours at 280°C in air.

1% Pt was added by incipient wetness impregnation, carried out by adding drop-wise a solution of $\text{Pt}(\text{NH}_2)_4(\text{NO}_3)_2$ dissolved in deionized water to the Cs-exchanged GeZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined at 280°C for 3 hours.

Before testing, the catalyst powder was pressed and sized to 20-40 mesh. 2.16 cm³ of the sized catalyst was mixed with 5.84 cm³ of inert silicon carbide chips and was pretreated at 460°C for 1 hour in flowing hydrogen.

CATALYST TESTING

Catalysts prepared by the procedures above were tested as follows:

Catalyst particles, mixed with inert silicon carbide chips, were loaded into a ½" OD plug reactor.

A synthetically-blended light naphtha was made by calculating a composition based on a PIONA analysis disclosed for a light naphtha in U.S. Patent no. 6,884,531, weighing out each component individually to obtain the desired mole fraction and mixing the components to make the feed mixture, which was vaporized into a stream of flowing hydrogen at a temperature of approximately 150°C. This gas mixture was passed through the reactor, which was maintained at the specified conditions in the tables below. The reaction products were analyzed by gas chromatography. Results are shown in the Table 1 below. The octane number increased from 51 for the naphtha feed to 95 for the reformat.

The octane number was estimated by using the pure component values for the research octane number (RON) and the motor octane number (MON) from ASTM Special Technical Publication #225, "Knocking Characteristics of Pure Hydrocarbons". A numerical average [(RON

+ MON)/2] of each component was weighted by volume to estimate the octane number of the feed and of the reformat.

compound	(RON + MON)/2	vol % in feed	vol % in reformate
n-hexane	25	51.8%	5.2%
2-methylpentane	73	15.4%	11.0%
3-methylpentane	74	20.2%	10.0%
2,3 dimethylbutane	99	3.2%	3.4%
2,2 dimethylbutane	93	2.1%	2.6%
Methylcyclopentane	86	3.4%	4.0%
Cyclohexane	80	2.6%	0.0%
1-hexene	70	0.0%	1.4%
2- and 3-hexene	87	0.0%	4.7%
2-MP related olefins	91	0.0%	4.4%
3-MP related olefins	89	0.0%	8.5%
MCP related olefins	84	0.0%	2.8%
Benzene	123	1.4%	38.5%
n-pentane	62	0.0%	0.9%
Isopentane	91	0.0%	0.5%
n-butane	87	0.0%	1.7%
Isobutene	95	0.0%	0.3%

Table 1: Change in composition due to reforming.

Catalyst: 1% Pt/CsGeZSM-5

LHSV = 2.0, T = 525°C, P = 1 atm.

H₂/hydrocarbon molar feed ratio = 0.45

Estimated octane number of feed naphtha is 51

Estimated octane number of reformate is 95

Concentrations of low octane components, such as n-hexane, 2-methylpentane and 3-methylpentane, have been decreased from 87.4% to 26.2%. The concentrations of high octane components has increased (2,2 and 2,3-dimethylbutane: 5.3% to 6.0%, benzene: 1.4% to 38.5%, n-butane, isobutene and isopentane: 0.0% to 2.5%, cyclic and branched olefins, such as 2-methylpentane related olefins, 3-methylpentane related olefins, methylcyclopentenenes and isobutene: 0.0% to 16.0%).

Fuel standards may limit the amount of olefins that are present in gasoline and may require that some or all of the olefins are hydrogenated to the corresponding paraffins. Table 2 shows the calculated composition and octane number of the product stream if all of the olefins were hydrogenated. The octane number would be increased from 51 for the naphtha feed to 89 for the reformat.

Compound	(RON + MON)/2	vol % in feed	vol % in reformat
n-hexane	25	51.8%	11.5%
2-methylpentane	73	15.4%	15.5%
3-methylpentane	74	20.2%	18.8%
2,3 dimethylbutane	99	3.2%	3.3%
2,2 dimethylbutane	93	2.1%	2.6%
Methylcyclopentane	86	3.4%	6.9%
Cyclohexane	80	2.6%	0.0%
Benzene	123	1.4%	38.0%
n-pentane	62	0.0%	0.9%
Isopentane	91	0.0%	0.5%
n-butane	87	0.0%	1.7%
Isobutene	95	0.0%	0.3%

Table 2: Change in composition due to reforming – product olefins hydrogenated

Catalyst: 1% Pt/CsGeZSM-5

LHSV = 2.0, T = 525°C, P = 1 atm.

H₂/hydrocarbon molar feed ratio = 0.45

Estimated octane number of feed naphtha is 51

Estimated octane number of reformat is 89

Because of its significant value as a chemical intermediate, benzene may be extracted from reformat. Table 3 shows the calculated composition and octane number of the reformat if all of the benzene were removed. The octane number would be increased from 51 for the naphtha to 78 for the reformat.

compound	(RON + MON)/2	vol % in feed	vol % in reformat
n-hexane	25	51.8%	8.5%
2-methylpentane	73	15.4%	17.9%
3-methylpentane	74	20.2%	16.3%
2,3 dimethylbutane	99	3.2%	5.5%
2,2 dimethylbutane	93	2.1%	4.3%
methylcyclopentane	86	3.4%	6.4%
cyclohexane	80	2.6%	0.0%
1-hexene	70	0.0%	2.3%
2- and 3-hexene	87	0.0%	7.7%
2-MP related olefins	91	0.0%	7.1%
3-MP related olefins	89	0.0%	13.7%
MCP related olefins	84	0.0%	4.6%
benzene	123	1.4%	0.0%
n-pentane	62	0.0%	1.5%
isopentane	91	0.0%	0.8%
n-butane	87	0.0%	2.8%
isobutane	95	0.0%	0.5%

Table 3: Change in composition due to reforming – benzene extracted for chemical use

Catalyst: 1% Pt/CsGeZSM-5

LHSV = 2.0, T = 525°C, P = 1 atm.

H₂/hydrocarbon molar feed ratio = 0.45

Estimated octane number of feed naphtha is 51

Estimated octane number of reformat is 78

It should be noted that even though there is no benzene in the product, the octane number

has increased. Therefore, the increase in octane number is not due only to the increase in aromatic content from aromatizing n-paraffins, but also from isomerizing n-paraffins to isoparaffins, further isomerizing isoparaffins to more highly branched isoparaffins, cracking n-paraffins to smaller n-isoparaffins and dehydrogenating both n- and iso- paraffins. Concentrations of low octane components, such as n-hexane, 2-methylpentane and 3-methylpentane, decreased and the concentrations of high octane components, such as 2,2 and 2,3-dimethylbutane, n-butane, isobutene, isopentane, 2-methylpentane related olefins and 3-methylpentane related olefins, and methylcyclopentenenes, increased. This data demonstrate that the process and catalyst of the present invention embodies mechanisms other than aromatization of paraffins.

The catalyst of the present invention may be in a series process with a conventional acidic reforming catalyst, such as a Group VIII metal on an oxide support, e.g., platinum deposited on alumina or silica to reform a hydrocarbon feed having a linear C₆-C₈ alkane content of at least 25%. The conventional acidic reforming catalyst may contain a promoter, such as rhenium, tin, cobalt, nickel, iridium, rhodium, ruthenium and combinations thereof. In one embodiment, the acidic reforming catalyst would be platinum and either rhenium or iridium deposited on alumina. Either catalyst may be the first catalyst in the series process. In one example, an acidic reforming catalyst comprising platinum deposited on alumina or silica is the first catalyst and a non-acidic medium pore or large pore zeolite comprising silicon, germanium and, optionally, aluminum on which a noble metal has been deposited comprising Pt/CsGeZSM-5 is the second catalyst.

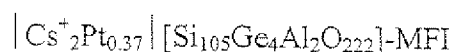
Numerous modifications and variations of the present invention are possible in light of the above teachings. It is to be understood that, within the scope of the appended claims, the invention may be practiced other than as specifically described.

WHAT IS CLAIMED AS NEW AND DESIRED TO BE SECURED BY LETTER OF PATENT OF THE UNITED STATES OF AMERICA IS:

1. A process for increasing octane number of a hydrocarbon feed comprising:
 - a) contacting at conditions for concurrently isomerizing n-paraffins to isoparaffins, further isomerizing isoparaffins to more highly branched isoparaffins, cracking n-paraffins to smaller n-isoparaffins, dehydrogenating both n-paraffins and iso-paraffins and dehydrocyclizing n-paraffins to aromatics a feed comprising naphtha having C₆-C₈ alkanes with a catalyst comprising a non-acidic medium pore or large pore zeolite comprising silicon, germanium and, optionally, aluminum on which a noble metal has been deposited; and
 - b) recovering a hydrocarbon product.
2. The process of Claim 1 wherein the zeolite is a medium pore zeolite.
3. The process of Claim 2 wherein the average pore size is in the range from about 5 to about 7 angstroms.
4. The process of Claim 1 wherein the zeolite has a Si/Al₂ atomic ratio of 40-500.
5. The process of Claim 1 wherein the zeolite has a Si/Al₂ atomic ratio of 50-150.

6. The process of Claim 1 wherein the germanium content of the zeolite is in the range from 1.0% to 10 % by weight.
7. The process of Claim 6 wherein the germanium content of the zeolite is from 3.5% to 6% by weight.
8. The process of Claim 1 wherein the noble metal is present in the range of from 0.05% to 3%.
9. The process of Claim 8 wherein the noble metal is present in the range of from 0.2% to 2%.
10. The process of Claim 9 wherein the noble metal is present in the range of from 0.2% to 1.5%.
11. The process of Claim 1 wherein the noble metal is platinum.
12. The process of Claim 1 wherein the zeolite is non-acidic by base-exchange with an alkali metal or alkaline earth metal.
13. The process of Claim 12 wherein the alkali metal is cesium present in a molar ratio to aluminum in the range from about 1 to about 2.

14. The process of Claim 1 wherein the contact between the alkane and the catalyst is at a liquid hourly space velocity in the range between 0.1 and 100 h⁻¹.
15. The process of Claim 1 wherein the contact between the alkane and the catalyst is at a temperature in the range between 200 and 600°C.
16. The process of Claim 1 wherein the contact between the alkane and the catalyst is at a liquid hourly space velocity in the range between 0.1 and 100 h⁻¹, at a temperature in the range between 200 and 600°C and at a pressure in the range between 1 and 315 psia.
17. The process of Claim 1 wherein the zeolite has an MFI structure.
18. The process of Claim 1 wherein the feed additionally contains sulfur up to 1000 ppm.
19. The process of Claim 1 wherein the catalyst is supported or bound.
20. The process of Claim 1 wherein the catalyst is of the formula:



21. The process of Claim 1 wherein the zeolite comprises additional elements of titanium, iron, gallium, boron or tin.
22. The process of Claim 1 wherein the catalyst is Pt/CsGeZSM-5.
23. The process of Claim 1 wherein the hydrocarbon feed comprises naphtha having at least 30% C₆-C₈ alkanes.
24. The process of Claim 1 wherein the hydrocarbon feed comprises naphtha having at least 40% C₆-C₈ alkanes.
25. The process of Claim 1 wherein the hydrocarbon feed comprises naphtha having at least 50% C₆-C₈ alkanes.
26. The process of Claim 1 wherein the feed additionally comprises higher and lower alkanes, isoparaffins, olefins, naphthenes and aromatics.
27. The process of Claim 1 wherein the feed additionally comprises pentane, nonane, decane and nonhydrocarbons which are catalytically nonreactive or inert.

28. A process for increasing octane number of a hydrocarbon feed comprising:

- a) contacting a hydrocarbon feed having a C₆-C₈ alkane content of at least 50% with a first catalyst at conditions to form a reformed product; and
- b) contacting the reformed product with a second catalyst; and
- c) recovering a hydrocarbon product,

wherein one catalyst comprises an acidic reforming catalyst comprising a Group VIII metal on an oxide support and

wherein the other catalyst is a non-acidic medium pore or large pore zeolite comprising silicon, germanium and, optionally, aluminum on which a noble metal has been deposited.

29. The process of Claim 26 wherein the acidic reforming catalyst comprises platinum deposited on alumina or silica.

30. The process of Claim 29 wherein the acid reforming catalyst additionally comprises rhenium, tin, cobalt, nickel, iridium, rhodium, ruthenium and combinations thereof.

31. The process of Claim 30 wherein the acidic reforming catalyst comprises platinum and either rhenium or iridium deposited on alumina.

32. The process of Claim 26 wherein the non-acidic medium pore or large pore zeolite comprising silicon, germanium and, optionally, aluminum on which a noble metal has been deposited comprises Pt/CsGeZSM-5.

33. The process of Claim 26 wherein an acidic reforming catalyst comprising platinum deposited on alumina or silica is the first catalyst and wherein a non-acidic medium pore or large pore zeolite comprising silicon, germanium and, optionally, aluminum on which a noble metal has been deposited comprising Pt/CsGeZSM-5 is the second catalyst.