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(72) Inventeurs/Inventors:
SHAMSHOUM, EDWAR S., US;
GHOSH, ASHIM K., US;
SCHULER, THOMAS R., US

(73) Propriétaire/Owner:
FINA TECHNOLOGY, INC., US

(74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : PROCEDE DE CONVERSION D'HYDROCARBURES
(54) Title: HYDROCARBON CONVERSION PROCESS

(57) Abrégé/Abstract:
A process is provided for the conversion of normal paraffins to their higher octane isomer counterparts and/or to isobutane. The hydrocarbon conversion catalyst is a platinum and lanthanum metal-loaded X zeolite. The process of the present invention comprises contacting the hydrocarbon feed containing normal C_5 to C_{12} paraffins with the hydrocarbon conversion catalyst under conversion conditions sufficient to convert the normal paraffins to their corresponding isoparaffins and/or to isobutane.

HYDROCARBON CONVERSION PROCESS

ABSTRACT

A process is provided for the conversion of normal paraffins to their higher octane isomer counterparts and/or to isobutane. The hydrocarbon conversion catalyst is a platinum and lanthanum metal-loaded X zeolite. The process of the present invention comprises contacting the hydrocarbon feed containing normal C_5 to C_{12} paraffins with the hydrocarbon conversion catalyst under conversion conditions sufficient to convert the normal paraffins to their corresponding isoparaffins and/or to isobutane.

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HYDROCARBON CONVERSION PROCESS

TECHNICAL FIELD OF THE INVENTION

This invention relates the use of a platinum metal-loaded X zeolite catalyst in a process for converting normal paraffins to their higher octane isomer counterparts and/or to isobutane.

BACKGROUND OF THE INVENTION

The isomerization of normal paraffins has long been an important refinery process. The resulting isomerization products have significantly higher octane values (RON) than their normal paraffin counterparts. For example, isomerization of normal heptane to methylhexanes and dimethylpentanes increases the RON value by approximately 50 and 90, respectively. Similarly, isomerization of normal octane to methylheptanes and dimethylhexanes results in an increased RON value of about 35 and 85, respectively. These higher octane isomerization products can then be blended with gasoline to increase its octane value.

Various catalysts have been employed to catalyze such isomerization reactions, including Friedal-Crafts catalysts (e.g. aluminum chloride), noble-metal catalysts, and crystalline aluminosilicate zeolite catalysts, such as zeolite X, Y, and synthetic mordenite. Further, zeolite-based bi-functional catalysts have also been used in hydroisomerization processes. The process operates at a relatively low hydrogen pressure owing to the high activity of the zeolite catalyst. Incorporation of a metal into the zeolite catalyst functions to dehydrogenate the normal paraffins to olefins. The olefins are then converted to carbocations on the acidic zeolite and desorbed as isoolefins, which are then hydrogenated again on the metal to give the corresponding isoparaffins.

Another important refinery process is the conversion of normal paraffins to more desirable products such as isobutane.

Isobutane is a valuable product that can be used to produce alkylates, or can be selectively dehydrogenated to isobutylene for use in MTBE (methyl tert-butyl ether) processes. Demand for high octane oxygenates such as MTBE, as well as for isoparaffins and alkylates, will likely increase in view of federal regulations requiring a reduction in the vapor pressure and aromatics content of gasoline.

It can be appreciated that, at any given time, the prevailing economic conditions will have a considerable impact on determining whether it is more desirable to isomerize a feedstock of normal paraffins to their higher octane isomer counterparts, or to convert them to isobutane. What would be advantageous, therefore, is a catalyst and process that could be used for the isomerization of normal paraffins and/or the conversion of normal paraffins to isobutane.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a novel process for converting normal paraffins to more valuable products, such as their higher octane isomer counterparts and/or isobutane. The present invention may be utilized to obtain high yields of liquid isomerization products having significantly higher octane (RON) values than the normal paraffin feed, while at the same time producing substantial amounts of isobutane. The process comprises contacting the normal paraffin feed with a hydrocarbon conversion catalyst under conversion conditions whereby the corresponding isoparaffins and/or isobutane are formed. The hydrocarbon conversion catalyst is a platinum metal-loaded X zeolite which has been fully ion-exchanged with lanthanum ions.

A platinum/lanthanum X (Pt/LaX) catalyst suitable for use in the present process is preferably prepared by first fully ion-exchanging a "parent" or as synthesized X zeolite with lanthanum ions and then ion-exchanging this lanthanum containing form of the zeolite with platinum ions. The platinum and lanthanum ion-exchanged zeolite is extruded with a binder, such as alumina or silica, and is then calcined. Alternatively, platinum can be incorporated into the catalyst by wet impregnation of the lanthanum X zeolite after it has been extruded with a binder.

As noted above, the present invention relates to a process for converting normal paraffins to their corresponding

isoparaffins and/or to isobutane. It is believed that isobutane formation occurs primarily as a result of hydrocracking of the isomerization products, but the isomerization of normal butane resulting from hydrocracking of the normal paraffin feed may also account for some isobutane production. The isobutane can then be selectively dehydrogenated to isobutylene and subsequently utilized to produce MTBE (methyl tertiary-butyl ether).

In another embodiment of the present invention, isobutane yields approaching 50% can be achieved by operating at higher conversion reaction temperatures. At such higher reaction temperatures, however, little or no liquid isomerization product can be recovered.

BRIEF DISCRIPTION OF THE DRAWINGS

FIGURE 1 is a graphical representation showing the octane values of hydrocarbons as a function of the number of carbon atoms per molecule.

DETAILED DISCRIPTION OF THE INVENTION

The present invention relates to a process for converting normal paraffins to their corresponding isoparaffins and/or to isobutane. FIGURE 1 graphically illustrates how such isomerization of normal paraffins increases the octane value of such hydrocarbons. The present process employs a hydrocarbon conversion catalyst comprising a platinum/lanthanum X (Pt/LaX) zeolite, having about 0.2 to 2.0 weight percent platinum and 5 to 12 weight percent lanthanum, with 0.4 to 1.2 weight percent platinum and 8 to 10 weight percent lanthanum being preferred.

In one embodiment a hydrocarbon feedstock containing normal paraffins is supplied to a reaction zone where it is brought into contact with a Pt/LaX zeolite conversion catalyst under conversion reaction conditions sufficient to cause isomerization of at least a portion of the normal paraffins, and thereby produce a liquid isomerization product having a RON value greater than that of the paraffin feed. Such an increase in the octane value of normal paraffins is obtained in accordance with the present invention without producing substantial amounts (i.e. less than 10 wt.%) of aromatic compounds.

Hydrogen is also supplied to the reaction zone, preferably as a co-feed with the hydrocarbon feedstock. Preferred hydrogen/hydrocarbon feed molar ratios are between about 1 and 10, with about 3 to 5 being more preferred. Conversion reaction conditions include a temperature of between about 190°C and 300°C, with about 220°C to 270°C being preferred and a pressure

between about 100 and 500 psig, with about 200 psig being preferred. Additionally, liquid hourly space velocities (LHSV) of between about 0.5 and 5.0 are utilized for the hydrocarbon feed with an LHSV of approximately 1 to 3 being most preferred.

The present invention has utility for conversion of hydrocarbon feedstocks containing normal C_5 to C_{12} paraffins. By practicing the process of the present invention, liquid yields (C_{5+}) of between 70 and 90 wt.% having RON values of betweeh about 55 and 40 respectively, can be obtained. The specific liquid yield and RON value is dependent primarily upon the reaction temperature, the selection of which may be governed by economic conditions. In addition to converting the normal paraffins to their corresponding isomers, significant amounts of isobutane will also be produced. Even when operating at conversion conditions most suitable for isomerization, isobutane yields up to about 15 to 20 wt.% can be obtained. If higher yields of isobutane are desired, higher conversion temperatures (e.g. 250 - 320°C, with 280 to 300°C preferred) are employed allowing yields of isobutane in excess of 40 wt.% to be obtained. At such higher temperatures, however, little or no liquid isomerization product can be recovered.

A Pt/LaX catalyst suitable for use in the present invention can be prepared by modification of a "parent" crystalline X zeolite having a silica to alumina molar ratio (SiO_2/Al_2O_3) of between about 1 and 3. Basic procedures for the preparation of such a "parent" zeolite X are well known in the art and need not

be detailed herein. In accordance with a preferred modification method, the parent X zeolite is first subjected to repeated lanthanum ion-exchanges to obtain the maximum loading of lanthanum ions in the zeolite. An aqueous solution of an inorganic lanthanum salt, preferably lanthanum nitrate, is employed as the ion-exchange medium. This lanthanum-containing form of the X zeolite powder is then subjected to platinum ion-exchange. Such platinum ion exchange is preferably accomplished by utilization of an aqueous platinum salt solution, such as tetraamineplatinum chloride.

After the platinum and lanthanum ions are incorporated into the X zeolite, it is then mixed with a binder, such as alumina sol, silica, gamma-alumina or other refractory oxides. This mixture is then pelletized by a suitable technique, such as extrusion, and the resulting pellets calcined at a maximum calcination temperature of 530°C. The resulting Pt/LaX zeolite preferably contains about 0.2 to 2.0 weight percent platinum and 5 to 12 weight percent lanthanum prior to extrusion with the binder, with 0.4 to 1.2 weight percent platinum and 8 to 10 weight percent lanthanum being preferred.

An alternative method for incorporating platinum into the catalyst is via wet impregnation of the lanthanum containing X zeolite after it has been extruded with a binder. Tetraamineplatinum chloride is preferably employed as the wet impregnation medium.

The following experimental work will serve to more fully describe the present invention. It is understood that these examples are not intended to limit the true scope of the invention, but rather are presented for illustrative purposes.

In experimental work carried out in accordance with the present invention, a Pt/LaX catalyst was employed for the conversion of a mixed feed containing approximately sixty percent normal heptane and forty percent normal octane to their corresponding isomers (iC_7 and iC_8) and/or to isobutane (iC_4).

Preparation of Catalyst

A parent, or "as synthesized" X zeolite was fully ion-exchanged with lanthanum ions in an aqueous solution of lanthanum nitrate. Three successive lanthanum ion-exchanges were employed to obtain a maximum lanthanum ion loading in the zeolite. The zeolite powder was then filtered, washed and dried. Platinum was ion-exchanged into the LaX zeolite powder utilizing an aqueous solution of tetraamineplatinum chloride. After filtration, washing, and drying, the Pt/LaX sample was extruded with twenty weight percent alumina as a binder and calcined at a maximum temperature of 530°C for two hours. The final catalyst contained 1.0 wt.% platinum and 9.98 wt.% lanthanum. The extruded catalyst had a SiO_2/Al_2O_3 molar ratio of 1.18.

Conversion of Normal Paraffins

The Pt/LaX catalyst prepared above was utilized in the conversion of a mixed hydrocarbon feed containing approximately sixty percent normal heptane and forty percent normal octane to their corresponding isomers (iC_7 and iC_8) and/or to isobutane (iC_4). Approximately 35 ml of the catalyst was loaded into a micro-reactor and activated by heating under hydrogen flow (0.4 L/min.), at a rate of 75°C per hour for the first two hours, followed by 50°C per hour until 350°C was reached. The system was left at this temperature overnight to complete activation. The temperature was then dropped to 190°C at which time the feed containing sixty percent n-heptane and forty percent n-octane was introduced at a rate to give a LHSV of approximately 1.7. A reaction pressure of 200 psig was utilized. Hydrogen was used as a co-feed and was adjusted to give an H_2/hydrocarbon feed molar ratio of approximately 4.6. The reactor temperature was increased by 10°C increments until the hydrocarbon feed was converted completely into gaseous products.

The results obtained are listed below in TABLE I.

TABLE I

Product Distribution of Normal C7 and C8 Conversion Over Pt/LaX Catalyst.

	Reactor Temperature/°C									
	197	213	227	233	238	243	249	254	260	265
Products, Wt.%										
i-butane	0.14	0.09	0.56	1.16	2.34	4.17	8.14	14.76	20.00	28.29
i-pentane	0.02	0.01	0.19	0.49	0.97	1.80	3.13	5.45	7.10	8.26
i-hexane	0	0	0.01	0.01	0.01	0.02	0.04	0.06	0.09	0.11
i-heptane	1.02	3.98	10.77	16.71	21.46	21.51	31.05	31.57	31.11	23.65
i-octane	2.64	8.37	18.06	22.90	24.31	23.41	19.33	11.43	6,04	1.60
aromatics	2.60	2.64	3.58	4.12	6.17	6.05	5.68	7.62	5.99	6.77
others	1.68	1.39	1.84	2.42	3.21	5.83	10.12	16.21	20.77	25.90
Unconverted Feed, Wt.%										
n-heptane	55.55	52.96	45.67	39.28	32.87	25.91	19.12	11.20	8.01	5.16
n-octane	36.35	30.56	19.32	12.91	8.66	5.30	3.39	1.70	0.89	0.26
C5+ Yield, Wt.%	98.23	98.58	97.94	97.26	95.92	92.54	85.47	73.83	64.74	50.47
RON (C5+)	3.53	6.76	15.28	22.21	29.36	36.15	42.53	52.99	58.05	64.85

A review of TABLE I indicates that the present invention can be utilized to give 70 to 90 weight percent liquid yields (C_{5+}) having RON values of approximately 55 and 40, respectively, at temperatures between 220°C and 250°C. In this temperature range, the isomerization product yields range between about 25 and 50 weight percent, and the iC_4 yield is 0.5 to 10 weight percent.

It can be seen that isobutane yields about 30 weight percent were obtained by operating at higher temperatures. At such high

temperatures, the liquid yield begins dropping rapidly and primarily gaseous products are produced.

Having described specific embodiments of the present invention, it will be understood that modification thereof may be suggested to those skilled in the art, and it is intended to cover all such modifications as falls within the scope of the appended Claims.

CLAIMS

1. A process for the conversion of normal paraffins comprising passing a hydrocarbon feedstream containing the normal paraffins through a reaction zone under conversion conditions effective to cause conversion of at least a portion of the normal paraffins to an isomerized hydrocarbon product, wherein

(1) the reaction zone contains a platinum/lanthanum X (Pt/La X) zeolite catalyst and
(2) the conversion conditions comprise:

(a) Temperatures in the range of 190°C to 300°C;
(b) Pressures in the range of 100 psig to 500 psig and
(c) Liquid hourly space velocities of the hydrocarbon feedstream between 0.5 and 5.0

2. The process as recited in Claim 1 wherein the normal paraffins have between 5 and 12 carbon atoms per molecule

3. The process as recited in Claim 2 wherein the normal paraffins have between 5 and 8 carbon atoms per molecule.

4. The process as recited in Claim 1 wherein hydrogen is supplied to the reaction zone as co-feed with the hydrocarbon feedstock at a hydrogen/hydrocarbon feedstock molar ratio between 1 and 10.

5. The process as recited in Claim 1 wherein a liquid C_{5+} hydrocarbon product yield of at least 70 weight percent, based upon the normal paraffin feed, is obtained.

6. The process as recited in Claim 5 wherein the liquid C_{5+} hydrocarbon product has a research octane number of at least 50.

7. The process as recited in Claim 1 wherein a liquid C_{5+} hydrocarbon product yield of at least 90 weight percent, based upon the normal paraffin feed, is obtained.

8. The process as recited in Claim 7 wherein the liquid C_{5+} hydrocarbon product has a research octane number of at least 30.

9. The process as recited in Claim 1 wherein at least a portion of the normal paraffins are converted to isobutane.

10. The process as recited in Claim 5 wherein at least a portion of the normal paraffins are converted to isobutane and an isobutane yield of at least 10 weight percent, based upon the normal paraffin feed, is obtained.

11. The process as recited in Claim 1 wherein the catalyst contains 0.2 to 2.0. weight percent platinum and 5 to 12 weight percent lanthanum.

12. The process as recited in Claim 11 wherein the catalyst contains 0.4 to 1.2 weight percent platinum and 8 to 10 weight percent lanthanum.

13. A process for converting normal paraffins to isobutane comprising passing a hydrocarbon feedstream containing the normal paraffins through a reaction zone under conversion conditions effective to cause conversion of at least a portion of the normal paraffins to isobutane, wherein

(1) the reaction zone contains a platinum/lanthum X (Pt/la X) zeolite catalyst and

(2) the conversion conditions comprise:

(a) Temperatures in the range of 250°C to 320°C;

(b) Pressures in the range of 689.7 kPa to 3448.3 kPa (100 psig to 500 psig); and

(c) Liquid hourly space velocities of the hydrocarbon feed between 0.5 and 5.0

14. The process as recited in Claim 13 wherein the normal paraffins have between 5 and 12 carbon atoms per molecule.

15. The process as recited in Claim 14 wherein the normal paraffins have between 5 and 8 carbon atoms per molecule.

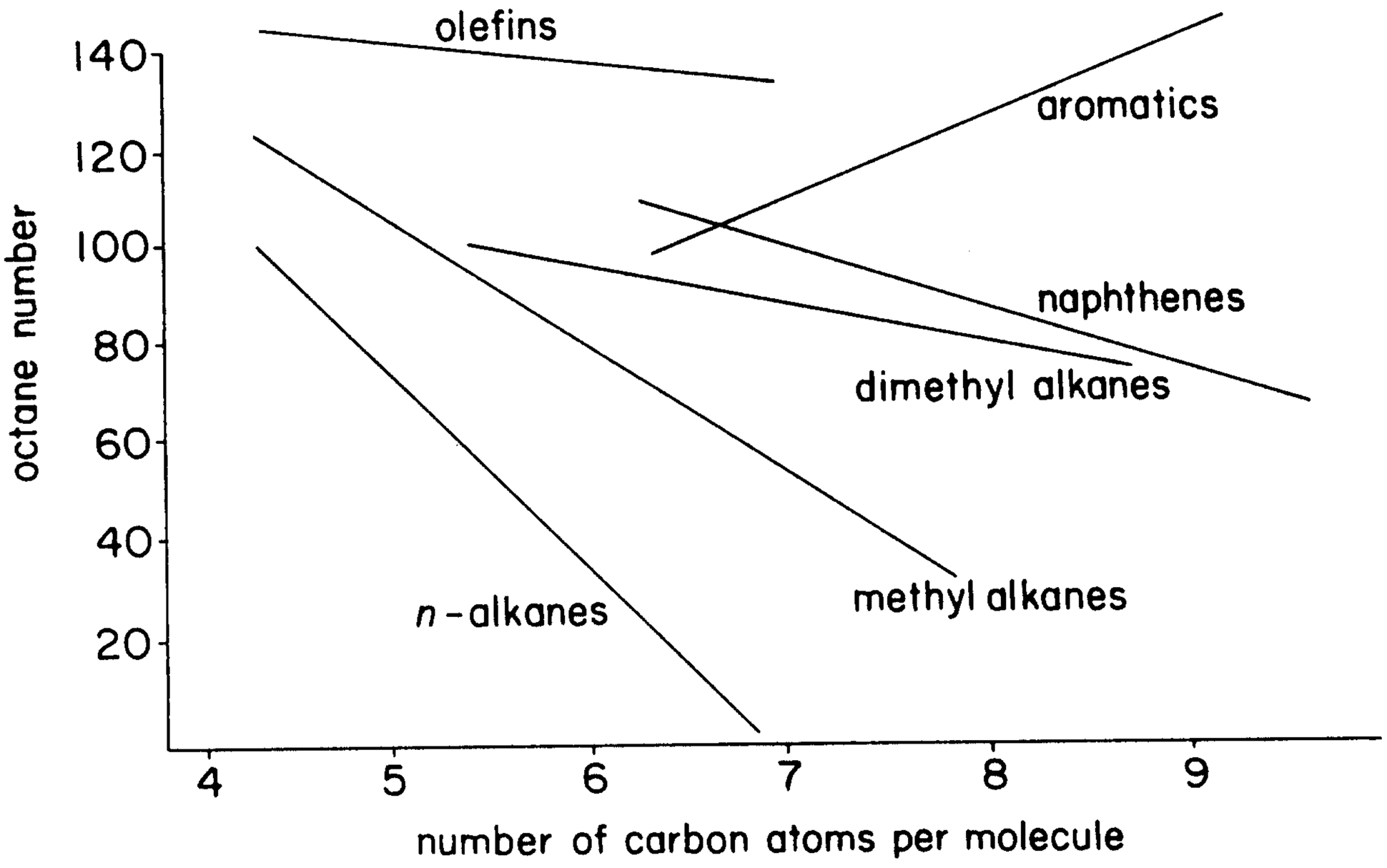
16. The process as recited in Claim 13 wherein hydrogen is supplied to the reaction zone as a co-feed with the hydrocarbon feedstock at a hydrogen/hydrocarbon feed molar ratio between 1 and 10.

17. The process as recited in Claim 13 wherein the weight percent yield of isobutane based upon the normal paraffin feed is at least 25.

18. The process as recited in Claim 13 wherein thy catalyst contains 0.2 to 2.0 weight percent platinum and 5 to 12 weight percent lanthanum.

19. The process as recited in Claim 18 wherein the catalyst contains 0.4 to 1.2 weight percent platinum and 8 to 10 weight percent lanthanum.

FIG. 1


olefins
aromatics
naphthenes
dimethyl alkanes
methyl alkanes
n-alkanes
140
120
100
80
60
40
20
octane number
4
5
6
7
8
9
number of carbon atoms per molecule