

- [54] **UPGRADING THE OCTANE VALUE OF NAPHTHA EMPLOYING A CRYSTALLINE ALUMINOSILICATE ZEOLITE WHICH HAS A HIGH SILICA TO ALUMINA RATIO WHEREIN ALUMINA IS INCORPORATED IN THE INTERSTICES OF THE ZEOLITE CRYSTAL**

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[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

Treatment and conversion of low octane, low aromatics content naphthas to both a substantially higher octane C₅ to 400°F fraction and a saturated LPG (C₃ + C₄ stream) product by relatively low temperature contact of such naphthas with a particular zeolite catalyst material in the absence of added hydrogen. The special catalyst comprises a zeolite having shape selectivity for monomethyl substituted paraffinic hydrocarbons, which has a high silica to alumina ratio of at least about 12, a constraint index of about 1 to 12, and a crystal density not substantially below about 1.6 grams per cubic centimeter and which, by reason of its composition, is eminently well suited to the upgrading of naphtha boiling range fractions by increasing the aromatics content thereof. This zeolite may have modifying metals, such as zinc, cadmium, etc., incorporated therewith in order to improve the aromatization activity thereof.

The instant improvement comprises providing aluminum, out of the crystal lattice of the zeolite, e.g., by exchange or impregnation and in addition to any which may be present in a matrixing component, along with the zeolite. It has been found that such aluminum significantly decreases the proportion of dry gas, C₁ + C₂, produced by this process.

7 Claims, No Drawings

**UPGRADING THE OCTANE VALUE OF NAPHTHA
EMPLOYING A CRYSTALLINE
ALUMINOSILICATE ZEOLITE WHICH HAS A
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ALUMINA IS INCORPORATED IN THE
INTERSTICES OF THE ZEOLITE CRYSTAL**

This invention relates to hydrocarbon conversion. It more particularly refers to a unique process for upgrading a low octane naphtha to a product comprising much higher octane gasoline and good quality liquifiable petroleum gas (LPG), e.g., a saturated $C_3 + C_4$ stream and a minimum of dry gas.

As used herein, the term low octane naphtha is intended to mean a petroleum cut having a boiling range within about C_5 to 400°F which contains less than about 30 volume percent aromatics and has a clear research octane number of up to about 65. This feed is usually a virgin straight run naphtha but other low octane naphtha boiling range petroleum fractions, such as for example, Udex raffinate, are suitable.

Octane upgrading of virgin naphthas by means of reforming with a platinum-alumina type catalyst is well recognized and widely practiced in the petroleum industry. This process predominantly dehydrogenates and isomerizes naphthenes to aromatics, isomerizes paraffins and dehydrocyclizes paraffins to aromatics. It is also known to improve the quality of reformates by subjecting them to shape selective cracking using a small pored zeolite in order to delete the remaining low octane normal paraffins from the reformat and therefore increase the octane number thereof at a small yield loss. Suitable catalyst for this process are erionite type zeolites and ZSM-5 type zeolites. Hydrogen is present during shape selective upgrading.

It is known to directly subject virgin naphtha to hydrocracking using a shape selective hydrocracking catalyst such as nickel ZSM-5 in the presence of added hydrogen in order to upgrade the naphtha to a higher octane hydrocrackate. This process is carried out at about 600° to 700°F and produces rather low yields (e.g., about 30 percent) of higher octane gasoline and large yields of LPG.

A recently developed process for upgrading naphtha envisions contacting the naphtha with a ZSM-5 type zeolite at about 650° to 1500°F in the absence of added hydrogen. This process converts a substantial portion of the feed naphtha to a highly aromatic liquid product, uses hydrogen generated by the aromatization to saturate $C_1 - C_4$ gases and produces a lesser proportion of LPG, and a large proportion of dry gas, that is C_1 and C_2 . It has been proposed to modify the catalyst used for this process in order to increase its aromatization activity by incorporating various metals, notably zinc or cadmium, therein by impregnation, exchange or otherwise. The process temperature is to some extent a function of the feed composition. Olefinic feeds can be treated at about 650°F and higher while paraffinic feeds can be treated at about 850°F and higher. Good operations with virgin naphthas are realized at about 900° to 1200°F.

It is an object of this invention to provide a novel process for upgrading naphthas.

It is another object of this invention to provide a novel process for converting virgin naphthas to a high octane liquid gasoline product and a quality LPG product without hydrogen consumption.

Other and additional objects of this invention will become apparent from a consideration of this entire specification including the claims hereof.

In accord with and fulfilling these objects, one aspect of this invention resides in a process of upgrading naphtha having a low aromatics content, and preferably a highly paraffinic naphtha, by a simultaneous aromatization and hydrocracking operation carried out at relatively limited reaction conditions with a special catalyst.

The catalyst used in this invention is based upon a synthetic aluminosilicate zeolite which was prepared utilizing an organic cation. This zeolite is shape selective for methyl substituted paraffins and smaller effective diameter molecules, has a silica to alumina ratio of at least about 12, preferably at least about 35-70, and has a constraint index of about 1 to 12, preferably about 2 to 7. The constraint index of a particular zeolite is determined by grinding the zeolite to the consistency of coarse sand; placing about one (1) gram thereof into a glass tube; treating the zeolite with air at 1,000°F for at least 15 minutes; flushing with helium while lowering the temperature to 550° from 950°F; replacing the helium with an equal weight mixture of n-hexane and 3-methyl pentane admixed with four (4) times its total moles of helium; passing this over the zeolite at a space velocity of 1 LHSV and atmospheric pressure for twenty (20) minutes; and sampling the effluent gas. The constraint index of the zeolite is the ratio of the logarithm of the fraction of n-hexane remaining divided by the logarithm of the fraction of 3-methyl pentane remaining. The zeolite should also preferably have a crystal density of not substantially below about 1.6 grams per cubic centimeter.

Zeolites as described and defined herein are suitably modified in a known manner to incorporate therewith zinc, or cadmium or other similarly behaving metals in order to enhance their aromatization activity.

Representative synthetic zeolites which conform to the above-identified parameters are ZSM-5, described in U.S. Pat. No. 3,702,886; ZSM-11, described in U.S. Pat. No. 3,709,979; ZSM-12, described in West German Offenlagunschrift Pat. No. 2,213,109; ZSM-21, described in U.S. application Ser. No. 358,192 filed May 7, 1973; and TEA mordenite, described in U.S. application Ser. No. 130,442, filed Apr. 11, 1971. The contents of these patents, applications and publication are incorporated herein by reference.

In accord with this invention, this metal modified zeolite is further modified in such manner as to surprisingly suppress the conversion of feed naphtha to undesirable dry gas ($C_1 + C_2$). This can be accomplished by incorporating aluminum with the zeolite. In this regard, it is to be understood that the aluminum referred to herein excludes aluminum in the crystal lattice of the zeolite and excludes aluminum in the form of alumina which is part of all of a matrixing material sometimes used in conjunction with zeolite catalysts. Rather, the aluminum referred to herein and forming an important part of this invention is interstitial aluminum, that is in the interstices of the zeolite crystal. This aluminum is suitably interstitially incorporated with the zeolite by conventional exchange, impregnation or vapor deposition techniques, with exchanged in aluminum being preferred. It is also within the spirit and scope of this invention to provide the interstitial aluminum by extracting such from the zeolite framework crystal by

means of suitable calcination procedures. For example, if the zeolite has a rather low silica to alumina ratio of about 35, calcination in a thick bed seems to provide a greater tendency for the crystal lattice to be dealuminized to some extent and at least part of the aluminum thus "freed" to deposit interstitially and thereby affect the dry gas make in the instant process. On the other hand, zeolites having a relatively high silica to alumina ratio of about 70 seem to dealuminize better upon calcination in a thin bed.

In any case, it is not really known or understood whether thick or thin bed calcination is better for incorporating aluminum according to this invention because, in addition to the silica to alumina ratio being an apparently important variable, the crystal size of the zeolite prior to calcination seems to affect the deposition of aluminum for the crystal lattice into the crystal interstices.

Suffice it to say that there are many known ways of incorporating interstitial aluminum with a crystalline zeolite, any or all of which appear to be pertinent to the practice of this invention.

Not only is it important to judiciously select the particular zeolite to be used as a catalyst for the instant process, it is similarly as important to modify the selected zeolite by incorporating therein an effective amount up to about 10 weight percent zinc and/or cadmium and an effective amount up to about 10 weight percent aluminum. Preferably at least about 0.4 weight percent of each of aluminum and zinc or cadmium are incorporated with the zeolite, and most preferably the incorporated proportion of both zinc or cadmium, and aluminum is up to about 7 weight percent. While the zinc or cadmium and aluminum can be incorporated by any known technique, such as for example, impregnation, exchange, vapor deposition or some combination thereof, it is preferred in the practice of this invention to utilize a zeolite having both zinc or cadmium and aluminum exchanged thereinto. In regard to the addition of modifying metals, the zeolite catalyst, it is interesting to note that the addition of zinc to a zeolite as described herein generally causes an increase in aromatization activity and selectivity of the zeolite. The addition of aluminum alone has not previously been reported as decreasing the aromatization activity and/or selectivity of these zeolites, yet the mixture of zinc or cadmium and aluminum utilized herein seems to have a synergistic effect in reducing conversion of the naphtha charge stock to aromatics increasing the conversion of the charge to LPG; decreasing the conversion of charge to dry gas; and producing a liquid product having at least as high or even higher research octane number and octane number improvement than when carrying out an aromatization conversion using the same zeolite modified only by incorporation of zinc.

The process of this invention is to be distinguished from previously described aromatization processes using a similar zeolite catalyst in that the operating temperature is generally lower, e.g., about 600° to 750°F, than would be used with a feed or comparable parafrinicity and the aromatics make is lower than the minimum 30 grams per 100 grams set forth in this prior work. It is similar to such aromatization process in that it operates at low space velocities of up to about 15 WHSV, preferably about 0.75 to 5 WHSV. It is also similar to such aromatization in that it neither desires

nor requires the co-feeding of hydrogen with the naphtha charge.

The process of this invention is to be distinguished from previously described hydrocracking processes using a similar zeolite catalyst in that while such hydrocracking process utilizes a high added hydrogen to hydrocarbon ratio and requires a hydrogenation/dehydrogenation component in the catalyst formulation, the process of this invention does not consume hydrogen nor does it require or desire a hydrogenation/dehydrogenation catalyst component. The instant process further differs from the prior hydrocracking process in that hydrocracking necessarily operated at substantial superatmospheric pressure whereas in this process it is desirable to operate at low or no pressure; this process is preferably operated at about atmospheric pressure.

This invention will be illustrated by the following Examples which are not considered to be limiting upon the scope hereof. Parts and percentages are by weight unless expressly stated to be on another basis.

EXAMPLE 1 (PRIOR ART)

A C₆ - 330°F Arabian straight run naphtha having a research octane number of 40 and a PONA analysis of:

Paraffins	63.5	WGT. %
Olefins	0	%
Naphthenes	20.1	%
Aromatics	16.4	%

was hydrocracked over a Ni ZSM-5 (0.68 percent Ni) catalyst at 660°F, 650 psig, 5 to 1 hydrogen to hydrocarbon ratio and a space velocity of 3 WHSV. Conversion was 69.3 percent. The liquid product had a C₅ to 400°F clear research octane of 91. The gas make (C₄-) was 61.8 percent of which 13.9 percent was isobutane and 1.2 percent was dry gas. The remaining 46.7 percent was LPG. No new aromatics were formed.

EXAMPLE 2 (PRIOR ART)

A refinery stream similar to that used in Example 1, C₅ - C₉, Udex raffinate, having a research octane of 61 and a PONA analysis of:

Paraffins	89.9	Wgt. %
Olefins	0	%
Naphthenes	3.4	%
Aromatics	6.7	%

was aromatized over a Zn ZSM-5 (7 percent Zn) catalyst at 800°F, 0 psig, 0 hydrogen and a space velocity of 1 WHSV. Conversion was 61.2 percent. The liquid product had a C₅ to 400°F clear research octane of 89. The gas make was 33.2 percent of which only 7.2 percent was isobutane and 4.5 percent was dry gas. LPG product accounted for 12.6 percent. New aromatics were made at a rate of 23.4 parts per 100 parts of charge.

EXAMPLE 3

The same refinery stream as used in Example 2 was processed according to this invention by passing it over an Al-Zn-ZSM-5 (3percent Al and Zn) at 700°F, 0 psig, 0 hydrogen and a space velocity of 1 WHSV. Conversion was 78.6 percent. The liquid product had a C₅ to 400°F clear research octane of 90. The gas make was 55.2 percent of which 13.9 percent was isobutane. So

far the same isobutane make as in Example 1, operating according to this invention made substantially more gasoline of almost equivalent octane number. As compared with Example 2, operating according to this invention made somewhat less aromatics (18.3 percent) and somewhat less hydrogen (0.25 percent vs. 0.79 percent) but made substantially more LPG and less dry gas. Since dry gas is the least valuable product produced in naphtha upgrading, a four fold reduction thereof from 45 percent of the product to 1.2 percent of the product makes this invention most valuable.

Example 3 was rerun with somewhat different modified catalyst. In the following Examples 4 through 6, the catalyst was a zinc exchanged ZSM-5 having a silica to alumina ratio of about 70 and a zinc content of about 0.8 percent.

Table 1

Example No.	Temp °F	Conversion %	C ₃ +R+O	Gas Make %	150-C ₄ %	C ₁ -C ₂ %
4	600	44.8	73.1	32.1	8.9	0.5
5	650	63.5	83.5	45.7	11.9	2.0
6	700	77.1	93.3	52.2	14.3	4.7

In the following Examples 7-10, the catalyst was an aluminum exchanged ZSM-5 having a silica to alumina ratio of about 35 and an aluminum content of about 0.8 percent.

Table 2

Example No.	Temp °F	Conversion %	C ₃ +R+O	Gas Make %	150-C ₄ %	C ₁ -C ₂ %
7	550	29.3	66.1	19.7	5.8	—
8	600	64.1	80.1	51.9	13.8	0.2
9	650	87.7	95.8	76.2	16.3	0.5
10	650	75.4	87.4	41.8	14.6	0.68(0.1=C ₂)

The following examples compare the results obtained from practicing this process with a ZSM-5 zeolite which has been respectively zinc exchanged and then thin bed calcined (TBC), zinc exchanged and then thick bed calcined (HBC), and aluminum and zinc exchanged (E). It also notes certain differences in results depending upon whether small(s) crystal size or large(l) crystal size zeolite was used:

Table 3

Example No.	S ₂ O ₃ /Al ₂ O ₃	Mod	Conversion %	C ₃ +R+O	Gas Make %	C ₁ +C ₂
11	70	TBC-1	63.5	83.5	42.6	2.0
12	70	HBC-1	67.6	85.6	46.0	2.3
13	70	E-1	72.3	86.2	53.7	1.4
14	70	TBC-s	71.3	86.1	49.6	1.7
15	70	HBC-s	72.4	85.9	51.6	1.9
16	70	E-s	73.9	87.6	54.2	1.4
17	35	TBC-1	72.6	86.9	52.5	1.6
18	35	HBC-1	74.5	88.1	56.4	1.2
19	35	E-1	77.0	89.8	56.5	1.1
20	35	TBC-s	75.9	89.7	55.2	1.7
21	35	HBC-s	75.2	90.1	53.8	1.5
22	35	E-s	78.2	90.3	57.8	1.5

What is claimed is:

1. In the process of upgrading the octane value of naphtha having a clear research octane number of up to about 65 by converting such at elevated temperature

in contact with an aromatization improving modified synthetic crystalline aluminosilicate zeolite having a silica to alumina ratio of at least about 12, a constraint index of about 1 to 12, and a crystal density of not substantially less than about 1.6 grams per cubic centimeter; the improvement, whereby increasing the production of saturated C₃ - C₄ LPG while maintaining production of higher octane gasoline having a clear research octane number of at least about 85, which comprises contacting said naphtha with said zeolite catalyst having aluminum incorporated into the interstices of the zeolite crystal about 600° to 750°F in the absence of added hydrogen at a space velocity of up to about 15 WHSV.

2. The improved process claimed in claim 1 wherein said zeolite is ZSM-5.

3. The improved process claimed in claim 1 wherein said aluminum is incorporated in proportions of up to about 10 weight percent.

4. The improved process claimed in claim 1 including

zinc in addition to aluminum both being present in a cumulative proportion of about 0.5 to 7 percent by weight.

5. The improved process claimed in claim 1 wherein said catalyst is ZSM-5 having zinc and aluminum exchanged thereinto.

6. The improved process claimed in claim 1 wherein said modified zeolite has a silica to alumina ratio of up

to about 70.

7. The improved process claimed in claim 1 wherein said aluminum is incorporated during calcining.

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