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3,206,525

PROCESS FOR ISOMERIZING PARAFFINIC
HYDROCARBONS

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This application is a continuation-in-part of applica-
tion Serial No. 851,526, filed November 9, 1959, and
now abandoned.

The invention relates to the isomerization of n-paraf-
finic hydrocarbons to obtain good yields of branched
chain aliphatic structures and is particularly concerned
with the catalytic isomerization of n-paraffinic hydrocar-
bons employing a hydrocarbon conversion catalyst con-
sisting essentially of a noble metal, an activity enhancing
compound and alumina. The branched chain aliphatic
structures, e.g. isomeric structures of n-paraffins, are par-
ticularly useful in providing gasoline components of high
octane rating.

In recent years automobile manufacturers have stead-
ily increased the compression ratios of their spark igni-
tion engines as a means of obtaining more power and
greater efficiency. As the compression ratios of the
engines increase, the hydrocarbon fuel employed must be
of higher octane rating to provide efficient knock-free op-
eration notwithstanding that fuel octane rating can be
increased through the addition of tetraethyl lead, and
other undesirable aspects of engine operation, for in-
stance pre-ignition, can be overcome by the use of other
additive components. Thus, the problem remains for
petroleum refiners to produce higher octane base hydro-
carbon fuels under economically feasible conditions.

These refiners now have installed a substantial number
of units for reforming straight run petroleum fractions
in the presence of free hydrogen and over a platinum
metal-alumina catalyst to obtain relatively high octane
products. Primarily these products, frequently called
reformates, are blended with other gasoline components
such as thermal and catalytically cracked gasolines, alkyl-
ates, etc., and additives such as tetraethyl lead in obtain-
ing present-day motor fuels. The reforming operation
has a number of disadvantages. First, as the octane rat-
ings of the blended engine fuels rise, the octane quality
of the reformate must also increase if the blends be other-
wise unaltered. This increase results in a substantial
reduction in yield particularly in obtaining reformates hav-
ing octanes (RON neat) of the order of 10 to 95 or
above. When the severity of the operation is increased,
the platinum metal-containing catalyst becomes fouled
more often with carbonaceous deposits which requires
more frequent regenerations or replacements. The plat-
inum metal-alumina catalysts are relatively expensive, and
either replacement or withdrawal from use during regen-
eration materially increases the cost of providing a given
volume of reformate. These and other factors affecting
the yield-octane number-cost relationship make it desir-
able for the refiner to consider various ways in which
high octane hydrocarbon fuel components can be ob-
tained by employing processing methods other than the
platinum metal-alumina catalyst reforming operation.

One method now under consideration by petroleum
refiners for obtaining stocks of higher octane value in-
volves the isomerization of C₄ or C₅ to C₉ n-paraffinic
hydrocarbons, that is, n-butane, n-pentane, n-hexane, n-
heptane, n-octane, n-nonane and their mixtures with each
other and with other hydrocarbons in the same approxi-
mate boiling range. In general, as the side chain branch-
ing of these n-paraffins increases, their octane ratings rise.
In the process of the present invention we have found

catalysts which are useful in the isomerization of the C₄
to C₉ n-paraffins in the presence of free hydrogen to afford
highly satisfactory yields of isomer products. These cata-
lysts are characterized by being sufficiently active to allow
the use of relatively lower isomerization temperatures
and provide for advantageous isomerization equilibrium
conditions.

The catalyst used in the process of the present inven-
tion includes catalytically effective amounts of a noble
or platinum group metal and activity enhancing or pro-
moting amounts of a component selected from the group
consisting of H₂SiF₆, NH₄BF₄ and Ni(BF₄)₂, supported
on an alumina base. The catalyst generally contains about
0.01 to 2 weight percent, preferably 0.1 to 1 weight per-
cent, of one or more of the platinum metals of Group
VIII, such as platinum, palladium, or rhodium. The
small amount of noble metal may be present in the metal-
lic form or as a sulfide, oxide or other combined form.
The metal may interact with other constituents of the
catalysts, but if during use the noble metal be present in
metallic form then it is preferred that it be so finely di-
vided that it is not detectable by X-ray diffraction means,
i.e. that it exists as crystals of less than 50 Angstrom
units size. Of the noble metals platinum, palladium and
rhodium are preferred.

The activity enhancing component is surface dispersible
on the support. It is employed in amounts sufficient to
enhance the life of the alumina support and such amounts
are, therefore, preferably added in direct proportion to
the area of the support. For instance, the amount of the
activity enhancing component will depend upon the spec-
ified promoting component employed. Generally, how-
ever, the activity enhancing component will be employed
in a molar ratio to the alumina of about 0.001 to 0.3:1
and preferably from about 0.02 to 0.1:1. When the
activity enhancing component contains boron and fluo-
rine, the molar ratio of the fluorine to boron will gener-
ally be from about 2 to 6:1. The weight percent of the
fluorine in the catalyst will generally be from about 0.1
to 15% and preferably from about 1.5 or 3 to 6 or 7.5
weight percent.

The noble metal and activity enhancing component
constituents of the catalyst are supported on an absorptive
alumina base of the activated or calcined type. The base
is usually the major component of the catalyst, generally
constituting at least about 75 weight percent on the basis
of the catalyst, preferably at least about 80 to 90%. The
catalyst base is an activated or gamma-alumina such as
those derived by calcination of amorphous hydrous alu-
mina, alumina monohydrate, alumina trihydrate or their
mixtures. The catalyst base precursor most advantage-
ously is a mixture predominating in, or containing a
major proportion of, for instance about 65 to 95 weight
percent, one or more of the alumina trihydrates bayerite
I, bayerite II (randomite) or gibbsite, and about 5 to 35
weight percent of alumina monohydrate (boehmite),
amorphous hydrous alumina or their mixture. The alu-
mina base can contain small amounts of other solid
oxides such as silica, magnesia, natural or activated clays
(such as kaolinite, montmorillonite, halloysite, etc.), ti-
tania, zirconia, etc., or their mixtures. Although the com-
ponents of the catalyst can vary as stated, a preferred
catalyst contains platinum and the activity enhancing
component deposited on activated alumina.

The isomerization reaction conditions used in the
method of the present invention include a temperature
sufficient to maintain the n-paraffin feed in the vapor
phase under the pressure employed. Generally, this tem-
perature will be from about 500 to 800° F., preferably
about 600 to 700° F. or 750° F., while the pressure will
be superatmospheric for instance ranging from about 50
to 1500 p.s.i.g., preferably about 200 to 1000 p.s.i.g.
The catalyst can be used as a fixed, moving or fluidized

bed or in any other convenient type of handling system. The fixed bed system seems most advantageous at this time and the space velocity will in most cases be from about 0.25 to 8:1, preferably about 0.75 to 4:1, weight of n-paraffin per weight of catalyst per hour (WHSV).

Free or molecular hydrogen must be present in our reaction system and the hydrogen to n-paraffin molar ratio will usually be from about 0.01 to 20:1 or more, preferably about 2 to 10:1. Conveniently, the hydrogen concentration is maintained by recycling hydrogen-rich gases from the reaction zone.

As previously stated the preferred catalyst base material is an activated or gamma-alumina made by calcining a precursor predominating in alumina trihydrate. An alumina of this type is disclosed in U.S. Patent No. 2,838,444. The alumina base is derived from a precursor alumina hydrate composition containing about 65 to 95 weight percent of one or more of the alumina trihydrate forms gibbsite, bayerite I and bayerite II (randomite) as defined by X-ray diffraction analysis. The substantial balance of the hydrate is amorphous hydrous or monohydrate alumina. Trihydrates are present as well defined crystallites, that is they are crystalline in form when examined by X-ray diffraction means. The crystallite size of the precursor alumina trihydrate is relatively large and usually is in the 100 to 1000 Angstrom unit range. The calcined alumina has a large portion of its pore volume in the pore size range of about 100 to 1000 Angstrom units generally having about 0.1 to about 0.5 and preferably about 0.15 to about 0.3 cc./g. of pore volume in this range. As described in the patent the calcined catalyst base can be characterized by large surface area ranging from about 350 to about 550 or more square meters/gram when in the virgin state as determined, for example, by the BET adsorption technique. A low area catalyst base prepared by treating the predominantly trihydrate base precursor is described in U.S. Patent No. 2,838,445. This base when in the virgin state has substantially no pores of radius less than about 10 Angstrom units and the surface area of the catalyst base is less than about 350 square meters/gram and most advantageously is in the range of about 150 to 300 square meters/gram.

The platinum group metal component of the catalyst can be added to the alumina base by known procedures. For instance, the platinum metal component can be deposited on a calcined or activated alumina, but it is preferred to add the platinum metal component to the alumina hydrate precursor. Thus, platinum can be added through reaction of a halogen platinum acid, for instance, fluoro-, chloro-, bromo- or iodo-platinic acid, and hydrogen sulfide in an aqueous slurry of the alumina hydrate. The hydrogen sulfide can be employed as a gas or an aqueous solution. Alternatively, the platinum component can be provided by mixing an aqueous platinum sulfide sol with the alumina hydrate. This sol can be made by reaction in an aqueous medium of a halogen platinic acid with hydrogen sulfide. The alumina hydrate containing the platinum metal can be dried and calcined usually at a temperature from about 750 to 1300° F. or more to provide the activated or gamma-alumina modifications. The activity enhancing component can be added to the catalyst in any stage of its preparation. It may be incorporated in the support, either before or after the addition of the Group VIII metal. It will usually be applied by impregnation from solution (water, organic or inorganic solvents) or from a gas phase. It is frequently added to the catalyst after it has been formed by tableting or extrusion and calcined. After the activity enhancing component is added in this procedure the catalyst can be recalcined.

Even though our catalyst can be employed directly in the isomerization system, it can be pretreated with free or molecular hydrogen. For instance, the catalyst can be heated at temperatures from about 800 to 900° F. in

a slowly flowing stream of hydrogen for a period of time (e.g. 1 to 3 hours) sufficient to activate the catalyst.

The catalyst employed in the process of the present invention can be regenerated employing conventional procedures, for instance by subjecting it to an oxygen-containing gas at temperatures sufficient to burn off carbon deposited on the catalyst during the conversion of petroleum hydrocarbon feedstock. This oxygen-containing gas, e.g. an oxygen-nitrogen mixture, can contain about 0.01 weight percent to 5 weight percent oxygen but preferably contains about 0.5 to 1.5 weight percent oxygen and is introduced at a flow rate such that the maximum temperature at the site of combustion is below about 1000° F.

The paraffinic feed material employed in our process is generally a C₄ to C₉ n-paraffinic-containing cut derived from crude petroleum hydrocarbons, as by distillation, reforming and extraction processes. The feed can be a blend of n-pentane and n-hexane usually containing about 25 percent or more of n-hexane and preferably a predominant amount of n-hexane.

The following specific examples will serve to illustrate our invention but they are not to be considered limiting.

Example I

PREPARATION OF NOBLE METAL ALUMINA CATALYST

A noble metal alumina composition of the kind described in U.S. Patent No. 2,838,444 can be employed in preparing the catalyst used in the process of our invention. The composition of this patent can be made as follows. Pure aluminum metal is dissolved in pure hydrochloric acid, and the resulting solution is mixed with deionized water to form an aqueous aluminum chloride solution and an alumina gel is prepared equivalent to approximately 65 grams of Al₂O₃ per liter. A separate deionized water solution of NH₄OH is prepared containing approximately 65 grams of ammonia per liter. These two reagents in approximate volume ratio of 1:1 are intimately mixed as a flowing stream at a pH of 8.0. The flowing stream is passed to a stoneware container and an alumina hydrate is visible. The precipitated hydrate is filtered from the mother liquid and washed to <0.2% chloride by successive filtrations and reslurryings in deionized water until the desired chloride concentration is reached. In each reslurrying ammonia is added to give a pH of about 9. The washed hydrate is covered with water in a container and aged at about 90° F. until it is approximately 70% trihydrate, the remaining being substantially of the amorphous or monohydrate forms. The total hydrate composition is comprised of 42% bayerite, 18% randomite, 11% gibbsite, 20% boehmite, and 9% amorphous as determined by X-ray diffraction analysis. The aged hydrate is mixed with deionized water in a rubber lined container to provide a slurry of about 7 weight percent Al₂O₃ at a pH of about 8.0. A chloroplatinic acid solution in deionized water (0.102 gram platinum per milliliter) is stirred into the slurry and the slurry is then contacted with a deionized water solution which has been saturated with H₂S at 78° F. to precipitate the platinum. The pH of the slurry is adjusted to 6.0 to 6.5 by ammonium hydroxide addition and the solids of the slurry are dried on a horizontal drum drier to give a powder of generally less than 20 mesh. The drum drier powder is mixed in a planetary type dough beater with sufficient deionized water to indicate 25 weight percent water on a Central Scientific Company Infra-red Moisture Meter containing a 125 watt bulb, Cat. No. 26675. The resulting mixture is forced through a die plate having holes 1/16" in diameter bolted to a 3/2" Welding Engineers screw extruder. The resulting strands are broken to particles of length varying generally between about 1/16" to 1".

The particles are dried at 230° F. and calcined by heating to 925° F. in a flow of nitrogen gas followed

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by a flow of air while the composition is maintained at a temperature in the range of 865° F. to 920° F. The composition thus produced analyzes about 0.6 weight percent of platinum which is in sufficiently divided form so as to exhibit by X-ray diffraction studies the substantial absence of crystallites or crystals of size larger than 50 Angstrom units. After the calcination the composition has an area (BET method) within the range from about 350 to 550 square meters/gram.

Example II

PREPARATION OF NOBLE METAL-NH₄BF₄-ALUMINA CATALYST

A platinum-alumina composition prepared essentially as described above in Example I, except that air was used for the complete calcination procedure, and containing about 0.6% platinum was employed in preparing the noble metal-NH₄BF₄-alumina catalyst by the following procedure. 209 grams of the calcined platinum-alumina composition were placed in a 1-liter 3-neck flask. The flask was connected through one neck to the house vacuum line and through another with a short length of "Tygon" tubing to a buret. The third neck was stoppered. The flask was evacuated and pumped with house vacuum for 10 minutes. 12.05 grams



(General Chemical technical grade ammonium fluoborate) were dissolved in DI water to make 170 ml. of solution which were poured into the buret. The solution was allowed to flow slowly into the flask while vacuum was still applied and the catalyst was shaken vigorously. When all the solution had been admitted, the vacuum was broken. The catalyst was transferred to a 6" crystallizing dish and dried in the forced air drying oven at 250° F. The catalyst was stirred occasionally while it was drying. The oven dry catalyst was placed in a cool muffle furnace, brought to 1000° F. and held at that temperature for 2 hours. The catalyst was then removed from the furnace and cooled in a desiccator. The catalyst analyzed 5.31% volatile matter (1000° C.), 0.57% B, and 3.71% F.

Example III

PREPARATION OF NOBLE METAL-H₂SiF₆-ALUMINA CATALYST

A platinum-alumina composition prepared essentially as described above in Example I, except that air was used for the complete calcination procedure, and containing about 0.6% platinum was employed in preparing the noble metal-H₂SiF₆-alumina catalyst by the following procedure. 209 grams of calcined platinum-alumina composition were placed in a 1 liter 3-neck flask. The flask was connected through one neck to house vacuum line and through another with a short length of "Tygon" tubing to a buret. The third neck was stoppered. The flask was pumped with house vacuum for 10 minutes. The H₂SiF₆ was diluted with DI water to make 170 ml. which were poured into the buret. The solution was allowed to flow slowly into the flask while vacuum was still applied and the catalyst was shaken vigorously. When all the solution had been admitted, vacuum was broken. The catalyst was transferred to a 6" crystallizing dish and dried in the forced air drying oven at 250° F. The catalyst was stirred occasionally while it was drying. The oven dry catalyst was placed in a cool muffle furnace, brought to 1000° F., and held at that temperature for 2 hours. The catalyst was then removed from the furnace and cooled in a desiccator. The catalyst analyzed 4.85 percent volatile matter (1100° C.) and 2.7 percent F.

Example IV

PREPARATION OF NOBLE METAL-Ni(BF₄)₂-ALUMINA CATALYST

A platinum-alumina composition prepared essentially as described above in Example I except that air was used

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for the complete calcination procedure, and containing about 0.6% platinum was employed in preparing the noble metal-Ni(BF₄)₂-alumina catalyst by the following procedure (Prep. 805-32II).

209 grams of the platinum-alumina composition were weighed into a 3-neck, 1 liter round bottom flask. One neck of the flask was stoppered, one neck attached to the closed stop-cock of a buret, and the third neck attached to a vacuum line. Ten minutes were allowed for removal of air from the flask and the catalyst. A solution of 16.7 g. of Ni(NO₃)₂·6H₂O and 12.05 g. of NH₄BF₄ dissolved in deionized water to make 170 ml. was then admitted through the buret. The flask and contents were shaken vigorously while the solution was being added. The catalyst was transferred to a 6" crystallizing dish and placed in a forced-air drying oven, set at 250° F., for about 16 hours. The oven-dried catalyst was placed in a sagger and heated in a muffle furnace 2 hours at 1000° F. The catalyst was cooled in a desiccator. Sample No. 500-K7030 Analysis: 1.49% Ni, 0.57% B, 3.02% F.

Example V

The isomerization process of the present invention is illustrated by Runs A, B, and C (illustrated below in Table I employing platinum as the Group VIII metal). A catalyst prepared essentially as described above in Example II was employed in Run A, a catalyst prepared essentially as described above in Example III was employed in Run B and a catalyst prepared essentially as described above in Example IV was employed in Run C. All runs were conducted under the conditions specified in the table which also shows the results of these runs.

TABLE I

Run.....	A	B	C
Sample No.....	500-7, 024	500-7, 038	500-7, 030
Catalyst.....	(1)	(2)	(3)
V. M. (1100° C.) percent.....	5.31	4.85	
F, percent.....	3.71	2.70	
B, percent.....	0.57		
Isomerization activity:			
Conditions—			
Feedstock.....			
Temp., ° F.....	650	650	650
Pressure, p.s.i.g.....	300	300	300
WHSV.....	3	2.9	3
H ₂ /HC mol ratio.....	3/1	3/1	3/1
Product.....			
i-C ₄	53.9	60.5	58.1
n-C ₅	45.8	38.2	
C ₁	0.26	1.26	

1 Pt-NH₄BF₄-alumina.

2 Pt-H₂SiF₆-alumina.

3 Pt-Ni(BF₄)₂-alumina.

The following data indicates that a platinum-alumina composition, prepared essentially as described above in Example I except that air was used for the complete calcination procedure, containing promoter components in a combination of F— and Si— or BF₄— provides better results in the isomerization of n-pentane than the results provided by using any of these components alone. The results are based upon the isomerization of n-pentane to isopentane under conditions, unless otherwise specified, including a temperature of 600° F., a pressure of 300 p.s.i.g., a hydrogen to hydrocarbon mole ratio of 3/1 and 1.5 WHSV. The data sets forth the particular promoter component employed with the platinum-alumina composition and the results when a particular component is employed. The relative activity is based upon a 0.6% platinum-alumina-3.23% boria catalyst (Cat. No. 480-279) as a reference standard and was calculated using the following formula in which K represents the reaction rate constants:

$$\text{Rel. act.} = \frac{\text{K for experimental catalyst at the operating temperature}}{\text{K for 0.6\% platinum-alumina-3.23\% boria catalyst at the same temperature}} \times 100$$

Selectivity and conversion were calculated according to the formulae:

$$\text{Selectivity to } i\text{-C}_5 = \frac{\text{mole per cent } i\text{-C}_5 \text{ in product}}{\text{Total conversion}} \times 100$$

Total conversion = 1 - mole percent n-C₅ remaining in the product

Data

Catalyst No.	Promoter		Total conversion, mole percent	Selectivity, mole percent	Relative activity percent ⁴
	Analysis	Component			
500-7,038	2.70% F, 0.6% SiO ₂ (est.)	H ₂ SiF ₆	¹ 61.6	¹ 98.0	465
-7,017	0.20% SiO ₂	SiO ₂	(²)	(²)	520
-7,030	1.5% Ni, 0.57% B, 3.02% F	Ni(BF ₄) ₂	⁴ 58.1	⁴ 98.2	100
480-279	3.23% B	B ₂ O ₃	27.9	100	100

- ¹ Evaluated at 680° F., 3 WHSV.
² Excessive demethanation at 650° F.
³ Reference Catalyst: No. 480-279.
⁴ Evaluated at 650° F., 3 WHSV.

What is claimed:

1. In a method of isomerizing a C₄-C₉ n-paraffinic containing hydrocarbon feed, the step comprising contacting said feed in the vapor phase with a catalyst at a temperature of about 500 to 750° F., superatmospheric pressure, and in the presence of free hydrogen, said catalyst consisting essentially of about 0.1 to 2% of a platinum group noble metal and NH₄BF₄ on an activated alumina, said component being present in an amount effective to enhance the activity of the catalyst.

2. The method of claim 1 in which the temperature is from about 600-700° F. and the n-paraffin is n-pentane.

3. The method of claim 1 in which the noble metal is platinum and is about 0.1 to 2% of the catalyst.

4. The method of claim 1 in which the activated alumina is derived by calcination of an alumina hydrate precursor consisting essentially of about 65 to 95% of alumina trihydrate and about 5 to 35% of a member selected from the group consisting of amorphous hydrous alumina, alumina monohydrate and their mixture and the activated alumina has an area of about 350 to 550 square meters per gram.

5. In a method of isomerizing a C₄ to C₉ n-paraffinic containing hydrocarbon feed, the step comprising contacting said feed in the vapor phase with a catalyst at a temperature of about 500 to 750° F., superatmospheric pressure, and in the presence of free hydrogen, said catalyst consisting essentially of about 0.01 to 2% of a platinum group noble metal and Ni(BF₄)₂ on an activated alumina, said component being present in an amount effective to enhance the activity of the catalyst.

6. The method of claim 5 in which the temperature is from about 600 to 700° F. and the n-paraffin is n-pentane.

7. The method of claim 5 in which the noble metal is platinum and is about 0.1 to 2% of the catalyst.

8. The method of claim 5 in which the activated alumina is derived by calcination of an alumina hydrate precursor consisting essentially of about 65 to 95% of alumina trihydrate and about 5 to 35% of a member selected from the group consisting of amorphous hydrous

alumina, alumina monohydrate and their mixture and the activated alumina has an area of about 350 to 550 square meters per gram.

9. In a method of isomerizing a C₄ to C₉ n-paraffinic containing hydrocarbon feed, the step comprising contacting said feed in the vapor phase with a catalyst at a temperature of about 500 to 750° F., superatmospheric pressure, and in the presence of free hydrogen, said catalyst consisting essentially of about 0.01 to 2% of a platinum group noble metal and NH₄BF₄ on an activated alumina, said NH₄BF₄ being present in a molar ratio with respect to said alumina of from about 0.001 to 0.3:1.

10. In a method of isomerizing a C₄ to C₉ n-paraffinic containing hydrocarbon feed, the step comprising contacting said feed in the vapor phase with a catalyst at a temperature of about 500 to 750° F., superatmospheric pressure, and in the presence of free hydrogen, said catalyst consisting essentially of about 0.01 to 2% of a platinum group noble metal and Ni(BF₄)₂ on an activated alumina, said Ni(BF₄)₂ being present in a molar ratio with respect to said alumina of from about 0.001 to 0.3:1.

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