STUDIES ON THE ISOMERIZATION ACTIVITY OF PURE n-ALKANES ON ACIDIC CATALYSTS

By

RENU PATHAK

AND

HARSHITA GUPTA

College of Engineering

University of Petroleum & Energy Studies

Dehradun

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By

Renu pathak

&

Harshita gupta

Under the guidance of

Dr. R.P.Badoni

Approved by

……………………………….

Dean

College of Engineering

University of Petroleum & Energy Studies

Dehradun

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(ISO 9001:2000 Certified)

CERTIFICATE

This is to certify that the work contained in this thesis titled “STUDIES OF ISOMERIZATION OF PURE N-ALKANES ON ACIDIC CATALYSTS” has been carried out by RENU PATHAK & HARSHITA GUPTA under my supervision and has not been submitted elsewhere for a degree.

R.P. Badoni
May 02, 2009

Dr. R.P.BADONI

College of Engineering

Date

Corporate Office:
Hydrocarbons Education & Research Society
3rd Floor, PHD House,
4/2 Siri Institutional Area
August Kranti Marg, New Delhi - 110 016 India
Ph.: +91-11-41730151-53 Fax : +91-11-41730154

Main Campus:
Energy Acres,
PO Bidholi Via Prem Nagar,
Dehradun - 248 007 (Uttarakhand), India
Ph.: +91-135-2102690-91, 2694201/ 203/ 208
Fax: +91-135-2694204

Regional Centre (NCR) :
SCO, 9-12, Sector-14,
Gurgaon 122 007
(Haryana), India.
Ph: +91-124-4540 300
Fax: +91-124-4540 330

Regional Centre (Rajahmundry):
GIET, NH 5, Velugubanda,
Rajahmundry - 533 294,
East Godavari Dist., (Andhra Pradesh), India
Tel: +91-883-2484811/ 855
Fax: +91-883-2484822

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Renu pathak (R040205054)

Harshita gupta (R040205024)

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CHAPTER 1: WHY ISOMERIZATION REQUIRED

1.1 Background

Environmental concern and the subsequent legislations on emissions demand the use of high quality fuels. In case of gasoline, the Lead phase out, limitations on aromatics with specific restrictions to benzene left a few options for alternative gasoline blends, where the recently adopted oxygenates such as MTBE too created ambiguity due to its contribution to ground water contamination. At the present scenario of gasoline, branched hydrocarbons gain much importance, as they are the only components left to give high octane without any emission problems. Abundant availability of naphtha (90-140°C cut) that mainly contains C_7+ hydrocarbons is a great source for the isomerization reaction. Hydro-isomerization of high sulfur, high olefinic FCC gasoline is also an interesting way to improve gasoline quality without loosing any octane. Even in the present refinery configuration, addition of isomerization catalyst in the catalytic reformer can improve the quality of gasoline.

Discovery of a suitable technology and catalysts which could convert the especially the n-paraffins in C_7+ range into isomers having 90+ RONC without cracking the hydrocarbons would be a boon to refiners and provide eco-friendly gasoline by minimizing olefines and aromatics. The aim of the project is to select a catalyst that is applicable for the isomerization of n-hydrocarbon by comparing isomerization activity of pure n-hydrocarbon on different acidic catalyst like triflouromethane sulfonic acid, mordinite catalyst, zeolite with high steam enchanced acidity.

The existing main processes for high-octane gasoline production are reforming and FCC. Catalytic reforming of S-R naphtha/ FCC naphtha/ cocker naphtha/ hydrocracked heavy naphtha which yields reformate having as high as 95-105 RONC with large percentage of aromatics. Although reformate is high-octane products, they typically contain over 60% aromatics, and their use in reformulated gasoline should therefore be limited. In addition, in order to decrease harmful vehicle emissions, the concentration of benzene in gasoline has also been limited in several countries by government regulations. Isomerization of paraffins larger than C_6 is one way to improve octane without increasing the aromatic or olefin content. n-C_7 has a research octane rating of 0, while 2-methyl hexane and 2,3-dimethyl pentane have research octane ratings of 53 and 93, respectively. C_7 paraffins are relatively abundant in naphtha, and their isomerization is a natural extension to existing C_5/C_6 isomerization.

Discovery of a suitable technology and catalysts which could convert the especially the n-parafins in C_7+ range (having RONC < 17) into isomers having 90+ RONC without cracking the hydrocarbons would be a boon to refiners and provide eco-friendly gasoline by minimizing olefines and aromatics.

Abundant availability of light naphtha (90-140°C cut) that mainly contains C_7+ hydrocarbons is a great source for the isomerization reaction.

CHAPTER 2: ISOMERIZATION

Catalytic isomerization process is used to convert n-parafin to isoparafin , which may be alkyalated to liquid hydrocarbons in the boiling range of motor gasoline. This process is also used to convert relatively low octane number paraffins contained in light straight run naptha and raffinate into the more desirable isoparaffins which may have higher octane number. Isoparaffins provide high octane components in the lower boiling end of motor gasolene. Isomerization reaction is mildly exothermic. It is a reversible first order reaction. It requires catalyst to obtain significant yield of isomers. The role of catalyst in isomerization is extremely important, since the equilibrium concentrations of branched isomers in the reaction products increases at lower temperatures. The intensity of unwanted side reactions diminishes at lower temperatures. For that reasons, isomerizing catalysts must ensure the optimal rate of reactions at as low temperature as possible. To prevent coke deposition on catalyst, isomerization is carried out at an elevated pressure in a hydrogen atmosphere.

The isomerisation process involves the transformation of one molecular structure into another (isomer) whose component atoms are the same but arranged in a different geometrical structure. Since isomers may differ greatly in physical and chemical properties, isomerisation offers the possibility of converting less desirable compounds into isomers with desirable properties, in particular to convert n-paraffins into iso-paraffins, thereby increasing the octane of the hydrocarbon stream. The main fields of application of isomerisation are:

- ISOMERISATION of normal butane into isobutane
- ISOMERISATION of pentanes and hexanes into higher- branched isomers

Since branched isomers have a higher antiknock quality than the corresponding linear paraffins, this form of isomerisation is important for the production of motor fuels. Though butane isomerisation has maintained its importance, present day interest isomerisation is specially focussed on the upgrading of fractions containing C5 Pentane and C6 Hexane for use as motor gasoline components. This application has been prompted by the world drive to remove the lead additives gradually from motor gasoline in order to reduce air pollution. The octane loss caused by the removal or reduction of lead antiknock additives can be compensated for by isomerisation of pentane/hexane paraffin fraction of the light gasoline fractions.

Isomerisation technology has also improved substantially due to the hard work of many technologist. In order to achieve the low temperature necessary to obtain an acceptable yield of isomers, the Catalyst systems used in the early units were based on aluminium chloride in some form. These catalyst systems, however, had the drawback of being highly corrosive and difficult to handle. In recent years, catalyst of a different type have come in use. These are solid catalysts consisting of a support having an acidic carrier and a hydrogenation function, frequently a noble metal. Modern isomerisation units utilise these dual- function catalysts and operate in the vapour phase and the presence of hydogen. For these reasons, these process are called hydro- isomerisation processes.

The first hydro- isomerisation unit was introduced nin 1953 by UOP, followed in 1965 by the first BP one, while in 1970 the first Shell hydro-isomerisation (HYSOMER) unit was started up. At present the following hydro-isomerisation processes are commercially available:

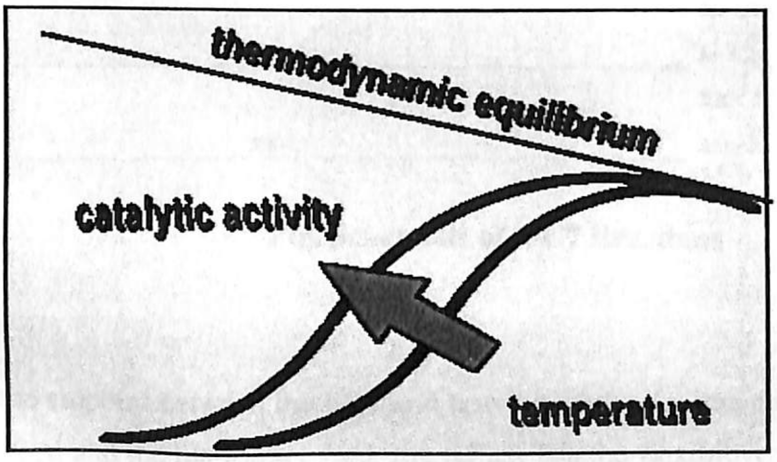
- UOP BUTAMER for butane isomerisation
- UOP PENEX for pentane/hexane isomerisation
- BP C_4 isomerisation for butane isomerisation
- BP C_5/C_6 isomerisation for pentane/hexane isomerisation
- SHELL Hysomer for pentane/hexane isomerisation

All these processes take place in the vapour phase on a fixed bed catalyst containing platinum on a solid carrier. As an example, the Shell Hysomer process will be briefly described. The liquid feedstock is pentane/hexane from light naphtha. Naphtha splitters are widely used to split naphtha into light naphtha, heavy naphtha and also LPG. The light naphtha (C5/C6) is combined with the recycle gas/ fresh gas mixture. The resultant combined reactor feed is routed to a feed/ effluent heat exchanger, where it is heated and completely vaporised by the effluent of the reactor. The vapourised combined reactor feed is further heated to the desired reactor inlet temperature in the reactor charge heater. The hot charge enters the Hysomer reactor at the top and flows downwards through the catalyst bed, where a portion of normal and mono- branched paraffins is converted into higher branched (high octane) components. Temperature rise from the heat of reaction release is controlled by a cold quench gas injection into the reactor. Reactor effluent is cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle gas stream returning to the reactor via the recycle gas compressor.

The catalyst is a dual function catalyst consisting of platinum on a zeolite basis, highly stable and regenerable. Temperatures and pressure vary in a range of 230 - 285 ^{0}C and 13-30 bar, C_5/C_6 content in product relative to that in feed is 97% or better, and octane upgrading ranges between 8 and 10 points, depending on feedstock quality. The Hysomer process can be integrated with catalytic reformer, resulting in substantial equipment savings, or with iso-normal separation processes which allows for a complete conversion of pentane/hexane mixtures into isoparaffin mixtures.

3.1 Thermodynamics of Isomerisation

Isomerization of paraffins is limited by thermodynamics. Low temperatures are therefore favored. High activity catalysts approach equilibrium conversion at lower temperature, leading to higher iso-paraffin yields.



Schematic of thermodynamics of Isomerisation

Nowadays many refiners are looking into the isomerisation processes to add potential extra value and complimentary to the platforming process. Directly both the platforming and isomerisation process work hand in hand in several ways. C5 paraffins tend to crack away in the platformer, but give high upgrading in the isomerisation unit. C6 components convert nicely to benzene in the platformer, but nowadays the specs on aromatics and benzene are tightening, which makes conversion of these components to C6 isomers preferred. Furthermore, benzene is hydrogenated in the isomerisation unit. C7 paraffin cracks into light paraffin and also give high end toluene and C7 isomers.

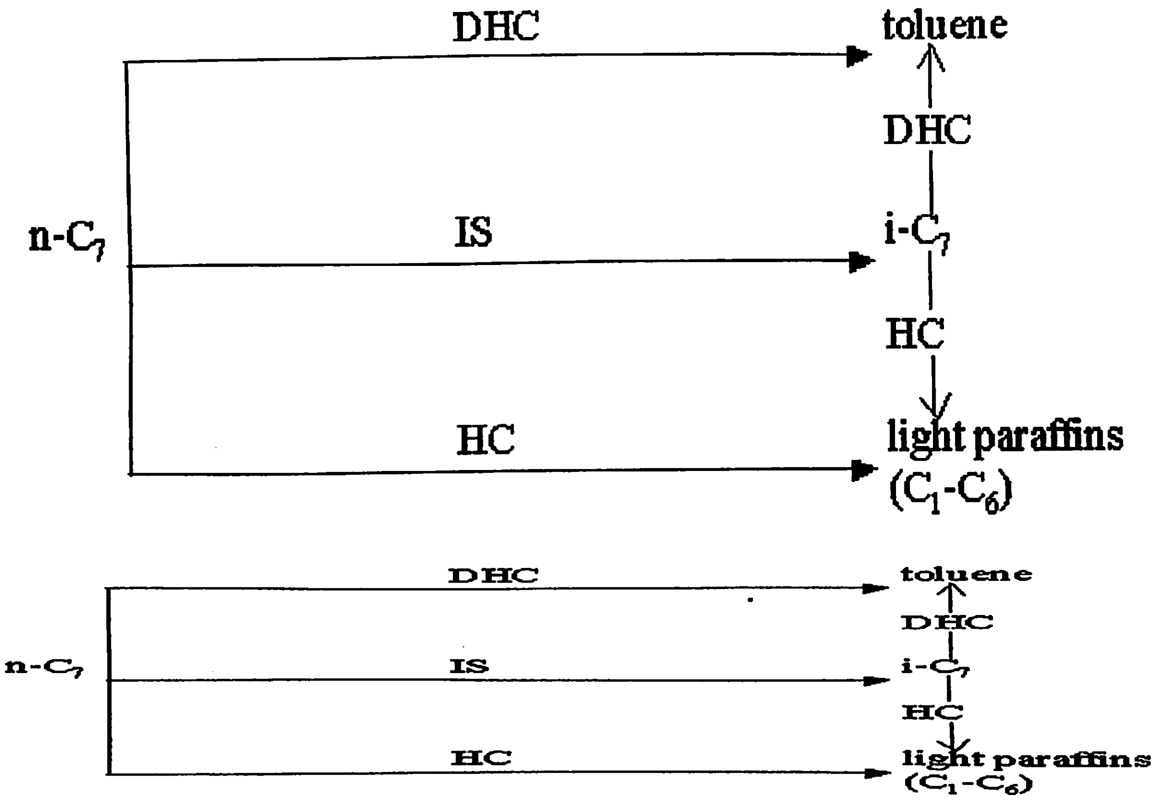


Fig. Schematic of n-C7 Reactions

By adjusting the cutpoint between the light and heavy naphtha, i.e. the cutpoint between the feed to the isomerisation feed and the platformer feed, the refiner has the flexibility to control the benzene content of its gasoline pool.Catalytic hydro-isomerization of paraffines takes place under medium pressure (typically 30 bar) in a hydrogen atmosphere.

CHAPTER 3: CONCEPT OF OCTANE NUMBER

The **octane rating** is a measure of the auto ignition resistance of gasoline (petrol) and other fuels used in spark-ignition internal combustion engines.

3.1 Knock Resistance

Engine knocking is compression detonation of fuel in the power stroke of the engine. Knocking occurs when the air-fuel mixture autoignites all at once (or sometimes perhaps when the flame front goes supersonic because of early ignition timing), before the flame front from spark plug ignition can reach it[11]. The explosive reaction causes combustion to stop before the optimum timing, causing a decrease in performance. A fuel, such as ethanol, with a high auto ignition temperature that burns reasonably fast and thus does not need early ignition timing will most often have high practical value knock resistance.

3.2 Definition of Octane Rating

Octane is measured relative to a mixture of isooctane (2, 2, 4-trimethylpentane, an isomer of octane) and n-heptane. An 87-octane gasoline, for example, has a mixture of 87 vol-% isooctane and 13 vol-% n-heptane. This does not mean, however, that the gasoline actually should contain these chemicals in these proportions. It simply means that it has the same auto ignition resistance as the described mixture.

A high tendency to auto ignite, or low octane rating, is undesirable in a gasoline engine but desirable in a diesel engine. The standard for the combustion quality of diesel fuel is the cetane number. A diesel fuel with a high cetane number has a high tendency to auto ignite, as is preferred.

3.3 Measurement Methods

The most common type of octane rating worldwide is the **Research Octane Number (RON)**. RON is determined by running the fuel through a specific test engine with a variable compression ratio under controlled conditions, and comparing these results with those for mixtures of isooctane and n-heptane.

There is another type of octane rating, called **Motor Octane Number** (MON) or the aviation lean octane rating, which is a better measure of how the fuel behaves when under load. MON testing uses a similar test engine to that used in RON testing, but with a preheated fuel mixture, a higher engine speed, and variable ignition timing to further stress the fuel's knock resistance. Depending on the composition of the fuel, the MON of a modern gasoline will be about 8 to 10 points lower than the RON. Normally fuel specifications require both a minimum RON and a minimum MON.

	MON	**RON**
Inlet air temperature	148.9 C	65.6 C
Engine jacket temp	100 C	100 C
Engine RPM	900	600

In most countries (including all of Europe and Australia) the "headline" octane that would be shown on the pump is the RON, but in the United States and some other countries the headline number is the average of the RON and the MON, sometimes called the **Anti-Knock Index (AKI)**, **Road Octane Number (RdON)**, **Pump Octane Number** (PON), or **(R+M)/2**. Because of the 8 to 10 point difference noted above, this means that the octane in the United States will be about 4 to 5 points lower than the same fuel elsewhere: 87 octane fuel, the "regular" gasoline in the US and Canada, would be 91-95 (regular) in Europe.

The octane rating may also be a "trade name", with the actual figure being higher than the nominal rating. It is possible for a fuel to have a RON greater than 100, because isooctane is not the most knock-resistant substance available. Racing fuels, straight ethanol, Avgas and liquefied petroleum gas (LPG) typically have octane ratings of 110 or significantly higher - ethanol's RON is 129 (MON 102, AKI 116). Typical "octane booster" additives include tetra-ethyl lead and toluene. Tetra-ethyl lead is easily decomposed to its component radicals, which react with the radicals from the fuel and oxygen that would start the combustion, thereby delaying ignition.

Many high-performance engines are designed to operate with a high maximum compression and thus need a high quality (high energy) fuel usually associated with high octane numbers and thus demand high-octane premium gasoline. The power output of an engine depends on the energy content of its fuel, and this bears no simple relationship to the octane rating. A common myth amongst petrol consumers is that adding a higher octane fuel to a vehicle's engine will increase its performance and/or lessen its fuel consumption; this is mostly false—engines perform best when using fuel with the octane rating they were designed for and any increase in performance by using a fuel with a different octane rating is minimal.

Using high octane fuel for an engine makes a difference when the engine is producing its maximum power. This will occur when the intake manifold has no air restriction and is running at minimum vacuum. Depending on the engine design, this particular circumstance can be anywhere along the RPM range, but is usually easy to pin-point if you can examine a print-out of the power-output (torque values) of an engine. On a typical high-revving motorcycle engine, for example, the maximum power occurs at a point where the movements of the intake and exhaust valves are timed in such a way to maximize the compression loading of the cylinder; although the cylinder is already rising at the time the intake valve closes, the forward speed of the charge coming into the cylinder is high enough to continue to load the air-fuel mixture in.

When this occurs, if a fuel with below recommended octane is used, then the engine will knock. Modern engines have anti-knock provisions built into the control systems and this is usually achieved by dynamically de-tuning the engine while under load by increasing the fuel-air mixture and retarding the spark. Here is a white paper that gives an example: In this example the engine maximum power is reduced by about 4% with a fuel switch from 93 to 91 octanes (11 hp, from 291 to 280 hp). If the engine is being run below maximum load then the difference in octane will have even less effect. The example cited does not indicate at what elevation the test is being conducted or what the barometric pressure is.

For each 1000 feet of altitude the atmospheric pressure will drop by a little less than 1 in Hg (11 kPa/km). An engine that might require 93 octane at sea level may perform at maximum on a fuel rated at 91 octane if the elevation is over, say, 1000 feet. See also the APC article.

The octane rating was developed by the chemist Russell Marker. The selection of *n*-heptane as the zero point of the scale was due to the availability of very high purity *n*-heptane, not mixed with other isomers of heptane or octane, distilled from the resin of the Jeffrey Pine. Other sources of heptane produced from crude oil contain a mixture of different isomers with greatly differing ratings, which would not give a precise zero point.

3.4 MON and RON depend on Gasoline Composition

The octane number measured is not an absolute number but rather a relative value based on accepted standards. By definition, n-heptane has an octane number (RON and MON) of 0, while iso-octane (2, 2, 4-trimethyl pentane) is 100. Linear combinations of these two components are used to measure the octane number of a particular fuel. A 90%/10% blend of iso-octane/n-heptane has an octane value of 90. Any fuel knocking at the same compression ratio as this mixture is said to have an octane number of 90.

In general, RON values are never less than MON, although exceptions to this rule exist. For pure compounds the differences between RON and MON range from 0 to more than 15 numbers. Typical values for gasoline range hydrocarbons having boiling points between 30° and 350° F go from less than 0 to greater than 100 with the extreme values being generated by extrapolation. Table 8 summarizes actual RON and MON values for a variety of pure hydrocarbons.

In practice octane numbers do not blend linearly. To accommodate this, complex blending calculations employing blending octane numbers as opposed to the values for pure hydrocarbons are routinely employed. There is no universal blending program used industry wide. In fact, for a given oil company, blending calculations that are refinery specific are not uncommon. As an improvement over octane numbers of pure compounds, there are tabulations of blending octane numbers for both RON and MON. Summarized in Table 1, these numbers are measured by blending 20 vol.% of the specific hydrocarbon in 80 vol.% of a 60/40 iso-octane/n-heptane mixture. Although still not exactly indicative of the actual blending octane number for a specific gasoline composition, the blending octane numbers are more representative. In general, the blending octane numbers are greater than the corresponding pure octane number

3.5 General Rules Regarding Octane Number of Compounds

- Normal (n) paraffins have the least desirable knocking characteristics, and these become progressively worse as the molecular weight increases.
- Iso (i) paraffins and naphthenes have higher octane than corresponding n-paraffins.
- Octane number of i-paraffins increases as the degree of branching of the chain is increased.
- Olefins have markedly higher octane numbers than the corresponding paraffins.
- Aromatics are hydrocarbons with the highest octane number for the same number of carbon atoms.

Thus it is clear that in order to have a large increase in octane number, it is necessary to transform paraffins and naphthenes into aromatics.

In view of strong environmental restrictions on gasoline, the main thrust of technological research has been in the field of finding different options for:

***Lead phase out and octane enhancement**

***Reduction in sulfur and olefin content**

***Decrease in benzene and aromatic content**

***Reduced tailpipe and evaporation emissions**

Table 1: Octane Numbers of pure hydrocarbons

	Actual		Blending	
Hydrocarbon	RON	MON	RON	MON
PARAFFINS				
n-butane	93		113	114
n-pentane	62	62	62	67
2-methylbyutane	92	90	99	104
2,2-dimethylpropane	85	80	100	90
n-hexane	25	26	19	22
2,2-dimethylbutane	92	93	89	97
n-heptane	0	0	0	0
2,2-dimethylpentane	93	96	89	93
2,2,3-trimethylbutane	>100	>100	113	113
2,2,3-trimethylpentane	100	100	105	112
2,2,4-trimethylpentane	100	100	100	100
OLEFINS				
1-Pentane	91	77	152	135
2-Methyl-2 butene	97	85	176	141
3-Methyl-2 pentene	97	81	130	118
4-Methyl-2 pentene	99	84	130	128
2,2,4-trimethyl-1 pentene	>100	86	164	153
2,2,4-trimethyl-2 pentene	>100	86	148	139
AROMATICS				
Benzene	>100	>100	99	91
Toluene	>100	>100	124	112
O-Xylene	>100	>100	120	103
M-Xylene	>100	>100	145	124
P-Xylene	>100	>100	146	127
Ethylbenzene	>100	98	124	107
1,3,5-trimethylbenzene	>100	>100	171	137
Propylbenzene	>100	98	127	129
Isopropylbenzene	>100	99	132	124
NAPHTHENES				
Cyclopentane	101	85	141	141
Methylcyclopentane	91	80	107	99
Cyclohexane	83	77	110	97
Methylcyclohexane	75	71	104	84
O-Dimethylcyclohexane	81	79	85	83
M-Dimethylcyclohexane	67	64	67	65
P-Dimethylcyclohexane	68	65	66	63

Chapter 4: Project Objective

4.1 Background of the proposed work

To study the isomerization activity of pure n-hydrocarbon on different acidic catalyst. The proposed research work is aimed to isomerize normal paraffins to high-octane isoparaffins with controlled cracking. Similarly cyclo paraffins also would be converted to corresponding isoparaffins via ring opening isomerization. The process is thus aimed to take care of paraffins and naphthenes in the C_7+ hydrocarbon feed to yield environ-friendly gasoline by minimizing benzene and total aromatics

4.2 Isomerization of Paraffinic Hydrocarbons with Triflouromethane Sulfonic Acid

Trifluoromethanesulfonic acid, also known as triflic acid or TfOH, is a sulfonic acid with the chemical formula CF_3SO_3H . It is often regarded as one of the strongest acids, and is one of a number of so-called "superacids". Triflic acid is widely used especially as a catalyst and precursor in organic chemistry.

Paraffinic hydrocarbons are converted to other hydrocarbons by contacting with a catalyst comprising trifluoromethanesulfonic acid. In another embodiment, normal paraffins are isomerized with high selectivity to skeletal isomers containing the same number of carbon atoms by contacting same with a catalyst comprising trifluoromethanesulfonic acid and a Group Vb metal fluoride.

Description:

It is well known that the more highly branched isomers of the paraffinic hydrocarbons occurring in petroleum gasoline fractions are more valuable than the corresponding slightly branched or straight chain hydrocarbons because of their higher octane ratings. The demand for motor fuels of greater octane number has increased markedly as the automotive industry has provided gasoline engines with increasingly higher compression ratios to attain greater efficiency. One of the economically important ways in which the increased demands for high octane fuels can be met is through the isomerization of the light naphtha components of such fuels.

This invention relates to hydrocarbon conversion. In this processs either, paraffinic hydrocarbons are converted to other hydrocarbons by contacting the paraffinic hydrocarbons with a catalyst comprising trifluoromethanesulfonic acid or paraffinic hydrocarbons are isomerized by contacting the paraffinic hydrocarbons with a catalyst comprising trifluoromethanesulfonic acid and a Group Vb metal fluoride. In accordance with a further aspect, normal paraffins are isomerized with high selectivity to skeletal isomers containing the same number of carbon atoms by contacting the paraffins with a catalyst comprising trifluoromethanesulfonic acid and a Group Vb metal fluoride.

It may be generally stated that the isoparaffinic and branched chain paraffin hydrocarbons are of greater commercial value to the petroleum industry than the corresponding straight chain hydrocarbons. Thus, for example, 2,2-dimethylbutane has a higher octane rating than the isomeric normal hexane. Isobutane is more valuable than normal butane since the former can be used as a basis for the preparation of 8-carbon-atom, branched chain hydrocarbons by alkylation with-butylene. The isomerization of normal paraffin hydrocarbons into the corresponding branched chain homologs is well known. For effecting the isomerization, it is customary to employ certain metal halides, particularly aluminum chloride or aluminum bromide, in conjunction with certain promoters such as hydrogen chloride, hydrogen bromide, or boron fluoride.

Recently, strong acid systems such as solutions of fluorosulfonic acid and antimony pentafluoride have also been disclosed as useful isomerization catalysts. An important problem arising with the use of these highly active catalysts is that they promote side reactions such as cracking and disproportionation. These side reactions are particularly evident at high conversion conditions and lead to the formation of substantial amounts of undesirable light and/or heavy side products. Hence objective is to provide an improved hydrocarbon conversion process, to provide an isomerization process whereby high selectivity to skeletal isomers is achieved and to provide an improved isomerization process for the conversion,of-paraffinic hydrocarbons. A further objective of this is to provide an improved catalyst for hydrocarbon conversion and-isomerization. In accordance with this, a process for the conversion of paraffinic hydrocarbons to other hydrocarbons is provided which comprises contacting the hydrocarbons with a catalyst comprising trifluoromethanesulfonic acid. It has been found that trifluoromethanesulfonic acid alone effects the isomerization and cracking of paraffinic hydrocarbons such as normal hexane.

Further in accordance with this, it has been found that normal paraffins can be isomerized with high selectivity to branched isomers containing the same number of carbon atoms by contacting the hydrocarbons with a catalyst comprising trifluoromethanesulfonic acid and,a,Group-Vb-metalfluoride.

In accordance with one specific embodiment, n-hexane isomerizes to predominantly neohexane in the presence of a catalyst comprising trifluoromethanesulfonic acid and at least one of phosphorus pentafluoride, antimony pentafluoride and arsenic pentafluoride.

Trifluoromethanesulfonic acid has various advantages not possessed by known superacid catalyst systems including

(1) it has a much higher boiling point, hence less is lost on recycle in continuous operation.

(2) it does not attack glass so sight gages, etc. made of glass can be used.

(3) it is the strongest protonic acid known and hence smaller amounts of acid are effective.

The catalyst composition comprises trifluoromethanesulfonic acid alone or trifluoromethanesulfonic acid with a metal fluoride of a Group Vb element. Specific examples of these metal fluorides include antimony pentafluoride, arsenic pentafluoride and phosphorus pentafluoride, as well as mixtures thereof.

Suitable feeds for the purposes comprise normal and branched chain paraffinic hydrocarbons having from four to seven, inclusive, carbon atoms per molecule, and may be exemplified by normal butane, normal pentane, normal hexane, 2-methylhexane, 3-methylhexane, and mixtures thereof. While the feed can substantially comprise the purified paraffinic hydrocarbon stream, it is also contemplated that mixtures of various paraffinic hydrocarbons can be employed.

The reaction conditions for isomerization of the feed can be in the range of 0° to 100° C, usually 15° to 80° C, and pressures sufficient to maintain the hydrocarbon reactants and catalysts as liquid in the reaction zone, and the temperatures and pressures should be chosen accordingly. The time of contact is subject to wide variation, the length of residence time dependent in part upon the temperature and catalyst concentration employed. In general, reaction times ranging from about 5 minutes to 48 hours, preferably 15 minutes to about 2 hours, are employed. The mole ratio of paraffinic hydrocarbon to Group Vb metal fluoride forming the catalyst will generally be in the range 50:1 to 0.2:1, preferably 1:1 to 20:1. The mole ratio of trifluoromethanesulfonic acid to Group Vb metal fluoride catalyst will generally be in the range 100:1 to 0.2:1, preferably 1:1 to 20:1. The mole ratio of trifluoromethanesulfonic acid to paraffinic hydrocarbon when trifluoromethanesulfonic acid alone is used as the catalyst will generally be in the range 0.1:1 to 50:1, preferably 0.5:1 to 20:1.

The process is conducted as a batch or a continuous operation. The apparatus employed can be of a conventional nature and can comprise a single reactor equipped with sufficient stirring devices. Good agitation is important because the less dense paraffinic hydrocarbon layer is not miscible with the denser liquid acid phase. Unreacted reactants, catalyst and other products of the reaction can be separated from the desired product and from one another such as by distillation and returned in whole or in part to the isomerization zone. The resultant product can be further processed as by alkylation and the like or be employed directly as a high octane gasoline blending agent. The reaction zone is preferably constructed of materials which are resistant to corrosion by the catalyst. For example, the reactor can be a Monel lined reactor. It is preferred that the reaction be carried out under anhydrous conditions in an inert gas atmosphere. Trifluoromethanesulfonic acid fumes copiously upon exposure to air and the Group Vb metal halides are also hydrolyzed on exposure to atmospheric moisture.

Specific example:

Paraffinic hydrocarbons were isomerized to isoparaffins with liquid phase catalyst systems of the invention utilizing a Monel reactor. The procedure for carrying out the isomerization in a Monel reactor is set forth below.

The process runs were carried out in a 300 ml Monel reactor. The trifluoromethanesulfonic acid was charged under nitrogen to the reactor and cooled therein to approximately -40° C. In Examples II, III and IV hereinbelow the Group Vb metal halide was then added to the cold trifluoromethanesulfonic acid until the desired weight was obtained, followed by addition of the paraffin. The reactor was then capped and placed in a thermostated Eberbach reciprocating shaker for any desirable time at a specified temperature.

Workup involved cooling the Monel reactor in dry ice-acetone and then rapidly pouring the cold mixture into a polyethylene separatory funnel. The upper hydrocarbon layer was drained under nitrogen into a Fischer-Porter Aerosol compatibility bottle containing about five grams of potassium carbonate and cooled in a dry ice-acetone bath. The bottle was quickly capped with a head bearing a pressure gage and a silicone septum for withdrawing samples for glc analyses. Results are reported in terms ofselectivities based on the glc analyses

4.3 Mordenite catalyst

Ammonia exchanged large port mordenite, which is subsequently mildly acid leached, and calcined, in which at least 95% of the exchangeable sodium has been removed and having from 0.38 to 0.8 milliequivalents of acid sites at least as strong as 48% sulfuric acid per gram (as measured by titration with butylamine, and employing dicinnamalacetone indicator) has been found to be a highly active hydrocarbon isomerization catalyst. Incorporation of noble metal, e.g. palladium, on the catalyst improves the selectivity for isomerization of normal pentane to isopentane for highly active catalysts at high conversion rate

Description:

An improved zeolite catalyst of high acidity for reactions such as the isomerization of normal hydrocarbons, and methods of making and using are there. Other reactions for which highly acid catalysts are desireable are alkylation and cracking of hydrocarbons. The use of large port hydrogen exchanged mordenite as a catalyst for hydrocarbon isomerization. The first named patent discloses that strong, hot acid leaching followed by mild acid leaching, finally followed by ammonium exchange results in an improved isomerization catalyst as compared to mordenite in which one or more of the 3 steps of the treatment is omitted.

The process involves ammonium exchange of large port mordenite followed by mild acid treatment. Such treatment results in a catalyst more active and selective toward hydrocarbon isomerization than previously known mordenite catalysts. Incorporation of a noble metal into the catalyst further improves its selectivity. As synthesized the material may be in the sodium exchanged form. Other exchange forms however may be employed, the sodium form being employed in the following example merely because it is the commonly available starting material. The ammonium exchange is preferably done with 3 to 5 normal NH_4+ solutions at room temperature or at elevated temperatures until 95% or more of the Na^+ has been removed. The acid treatment requires 0.1 to 1 N mineral acid at boiling (refluxing) temperature for 1 to 24 hours, preferably for 3 to 5 hours before the product is washed free of acid.

The acid treatment should be such that the silica to alumina ratio of the product is no higher than 17 to 1. The acidity of the zeolite after being washed with water and dried, subsequent to the acid treatment, can be measured by the use of dicinnimalacetone indicator and n-butylamine titrant as described by H. Benesi, J. Phys. Chem. 61, 970 (1957). The treated mordenite of this invention has been found by this method to have a total acidity of acid sites at least as strong as 48% sulfuric acid of from 0.38 to 0.8 milliequivalents per gram (pK_a of minus 3 or lower).

Example of specific embodiments

Example I

The starting material in the following example was large port sodium mordenite, made according to the teaching of U.S. Pat. No. 3,436,174, in pelletized form bonded by a silicious bond. The 1/16" pellets contained 6.1% Na_2O, and the silica to alumina mole ratio was 10.5 to 1.

The sodium zeolite was treated with 3 to 5 normal NH_4NO_3 solutions until chemical analysis showed a constant 0.27% by weight of Na_2O (on an anhydrous basis). The product was washed free of NH_4NO_3 solution by repeated washings with water. Two hundred grams of the washed product was treated by boiling for four hours in 400 ml. of 0.5 normal HCl. After washing free of acid, the product was found to contain 0.23% Na_2O, and has a silica to alumina ratio of 10.7 to 1, after calcination for 24 hours at a maximum temperature of 550° C. The testing procedure for isomerization employed a 1 to 1 by volume mixture of the mordenite pellets with inert fused alumina aggregate. The process conditions were a temperature of the bed of 480° F., pressure of 450 p.s.i.g., hydrogen to normal pentane feed mole ratio of 7/1 and weight hourly space velocity of 1.00 gram of normal C-5 per gram of catalyst per hour. The product of this example gave a 30.9% molar conversion to isopentane with 1.62% of the feed cracked (isomer ratio of 0.315, and selectivity 95%).

Example II

Sodium mordenite high purity powder (large port mordenite as disclosed in U.S. Pat. No. 3,436,174) was subjected to a plurality of 3 normal NH_4NO_3 exchanges until the soda content was less the 0.1% by weight (on an anhydrous basis). The silica to alumina mole ratio was 10. The washed ammonium exchanged mordenite was then refluxed for 3 hours in 0.5 N HCl, washed free of acid, and calcined as in Example I. The silica to alumina ratio of the product was 13, and the total acidity of acid sites stronger than 48% H_2SO_4 was 0.38 milliequivalents per gram. This product was re-exchanged with NH_4NO_3 and palladium was introduced by treatment with aqueous tetra-amino palladium chloride, to incorporate about 0.5% by weight of Pd.

Under the same test conditions as Example I this catalyst bonded with 20% by weight of microcrystalline boehmite and calcined as in Example I gave an isomer ratio (fraction of isopentane to C_5's in product) of 0.347 at 97.4% % selectivity (iso C_5 in product as % of C_5 converted), equivalent to a 34.4% conversion and 0.8% cracking of the feed.

Example III

Ammonium exchanged mordenite, prepared as in Example II was refluxed 3 hours in 0.34 normal nitric acid, to a silica to alumina ratio of 15.6. After washing and re-ammoniation, 0.5 weight % of palladium was incorporated by tetra ammonium palladium chloride exchange. The powder was then pelletized as in Example II.

The acidity equal to or greater than 48% H_2SO_4 was 0.517 meq/gram of mordenite, and when tested for pentane isomerization it gave 44.2% conversion, and, 0.6% cracking, to give an isomer ratio of 0.445 and a selectivity of 98.6%. The isomerization conditions varied slightly from the previous test in that the hydrogen to hydrocarbon mole ratio was 7.1 to 1, and the space velocity was 1.00 cc of normal pentane per cc of catalyst per hour (LHSV= 1).

When this catalyst was tested under conditions more amenable to commercial usage, i.e. T= 500° F., $H_2/C_5 = 1.8$, LHSV= 1.00, conversion of 64.7%, and cracking of 3.4% was obtained. This corresponds to an isomer ratio of 0.67 and a selectivity of 95%.

4.4 Isomerization of Paraffin Hydrocarbons Using Zeolites with High Steam-Enhanced Acidity

A process is provided for effecting hydroisomerization of a C_4-C_8 paraffin by contacting the same under hydroisomerization conditions with a catalyst comprising a porous crystalline zeolite characterized by a silica/aluminum mole ratio of greater than 12 and a constraint index within the approximate range of 1 to 12, which zeolite has undergone controlled pretreatment by contact with water to enhance the acid activity thereof, expressed as alpha, to greater than about 300. The catalyst also comprises, intimately combined therewith, a minor proportion of a Group VIII metal.

Description

This invention relates to a process for effecting isomerization of paraffins, including normal paraffins and/or cycloparaffins, in the presence of hydrogen and a catalyst comprising a highly siliceous porous zeolite crystalline material of controlled enhanced acid activity characterized by a silica/alumina mole ratio of greater than about 12 and a constraint index, hereinafter defined, within the approximate range of 1 to 12, which zeolite has intimately combined therewith a minor proportion of a Group VIII metal. It has here to for been known that the isomerization of paraffins, such as n-hexane, to equilibrium mixtures of branched chain isomers, substantially increases the octane rating of the paraffin hydrocarbons. Prior art processes dealing with paraffin isomerization include a liquid-phase process utilizing a catalyst containing an aluminum chloride dissolved in antimony trichloride, which, together with HCl formed during the reaction, are corrosive. Another process, referred to as the Penex process, which has been used for isomerizing pentane and hexane fractions from refinery naphthas and natural gasolines in the presence of hydrogen and a platinum containing catalyst requires the continuous addition to the feed of an organic chloride which also produces HCl. Another process involves reaction of a pentane/hexane feed in the presence of hydrogen and a catalyst containing platinum highly dispersed on hydrogen mordenite at a pressure of 150-350 psi and a temperature of 400 to 550 degrees F. with a maximum water level in the feed of 50 ppm. The above processes have been costly to operate because of extensive corrosive effects attributable to the use of highly acidic catalysts or by-products arising from use of such catalyst, thereby requiring expensive alloy equipment. Moreover, moisture and high molecular weigtt hydrocarbons usually present as contaminants in the charge stock cause deterioration of the catalyst and necessitate frequent replacement thereof. Another process which has been carried out at a higher temperature of 700 to 800 degrees F. utilizes a catalyst such as platinum on a silica-alumina base in the presence of hydrogen. At the high temperatures required, the equilibrium mixture of isomers is such that substantial recycling of a portion of the paraffin feed is necessary to obtain the desired improvement in octane rating.

Hydroisomerization of saturated aliphatic and cyclic hydrocarbons by contacting with a mixed dual-functional catalyst comprising hydrogen mordenite and a dehydrogenation component supported on a thermally stable carrier. One of the invention relates to hydroisomerization of paraffinic hydrocarbons in the presence of a mixed catalyst consisting essentially of an acid aluminosilicate portion and a hydrogenation component of a platinum metal supported on a thermally stable carrier. The present invention contemplates the upgrading of normal paraffinic hydrocarbons or cycloparaffins by hydroisomerization in the presence of a specified highly siliceous porous zeolite crystalline material of enhanced acid activity having a minor proportion of a Group VIII metal combined therewith.

In addition, the invention described herein involves continuous hydroisomerization of normal paraffins or cycloparaffins for extended periods of time in the presence of hydrogen and the above indicated catalyst so as to produce a mixture of branched chain isomers having a high octane rating without the use of corrosion resistant alloy equipment or frequent replacement of catalyst material. In addition, this invention is directed to the hydroisomerization of n-pentane, n-hexane or mixtures thereof in the presence of hydrogen and a specified catalyst comprising a porous crystalline zeolite of enhanced acid activity and defined silica/alumina mole ratio and constraint index and having a minor proportion of platinum, supported on an alumina carrier under specified reaction conditions.

In accordance with the present invention, it has been found that marked improvements are realized in a process for isomerizing paraffinic hydrocarbons admixed with hydrogen in the presence of a catalyst comprising a highly siliceous porous zeolite crystalline material having an acid activity, expressed as an alpha value, of at least about 300, generally in the approximate range of 300 to 10,000 and preferably between about 300 and about 5,000. The highly siliceous porous zeolite crystalline material employed is further characterized by a silica/alumina mole ratio of greater than about 12 and a constraint index, hereinafter defined, within the approximate range of 1 to 12, which zeolite has intimately combined therewith a minor proportion, generally in the range of 0.01 to 10 weight percent, of a Group VIII metal, which is preferably platinum or palladium. Isomerization of both, cycloparaffins such as cyclohexane to methyl cyclopentane, and isomerization of light paraffinic hydrocarbons of C_4, C_5 and C_6 paraffins and mixtures thereof has been effectively carried out with improved conversion and high selectivity to an iso-paraffin product.

Isomerization, in accordance with the present process, is carried out at a temperature between about 200 and about 900 degrees F., preferably between about 300 and about 750 degrees F., with a liquid hourly space velocity between about 0.1 and about 50, preferably about 0.2 and about 10 at a pressure between 0 and about 1,000 psig in the presence of an amount of hydrogen such that the hydrogen to hydrocarbon mole ratio is between about 0.1:1 and about 20:1. Enhancement in the acid activity of the above described process zeolite is achieved by treatment with water, i.e., liquid water or steam under controlled conditions

The conditions effecting enhancement of the porous zeolite depend on the interrelationship of several variables such as temperature, water partial pressure, treating time, nature of the zeolite and nature of treating gas. There exists a "zone of enhanced activity" where acid activity is increased over initial activity. Under conditions that are too mild, catalyst activation is not obtained. Alternatively, under too severe conditions, the catalyst will undergo deactivation. Under conditions of constant temperature, the following expression approximately describes the relationships of the two variables, treating time and water partial pressure:

$0.01(Pt)_T < (Pt) < 10(Pt)_T$

Where

$(Pt)_T = 2.6\times10^{-9}\, e^{16000}/T$;

P=Water Partial Pressure, atmospheres;t=Treating Time, hours;

T=Temperature, degrees K.

It has further been established that under the above controlled water treating conditions, ammonia addition to the water yields even higher activities than the treatment with water alone. The resulting hydrocarbon isomers produced by the process of the invention are useful as gasoline blending stocks because of their high anti-knock properties. In addition, isomerization of n-butane to isobutane provides the latter for olefin alkylation units, another source of high octane gasoline.

Description of specific embodiments

Following the teachings of the present invention, a hydrocarbon feed stock containing C_4 to C_8 paraffins, e.g., C_4 -C_6 normal paraffins, or cycloparaffins, such as cyclohexane, is contacted under hydroisomerization conditions with a catalyst comprising a porous zeolite characterized by a silica/alumina ratio of greater than about 12 and a constraint index within the approximate range of 1 to 12, which zeolite has undergone a controlled pretreatment to enhance the acid activity thereof, so that its acid activity, expressed as alpha value is greater than about 300, and which contains a Group VIII metal incorporated ther in.

Feedstocks employed in the present process include straight run C_4, C_5, C_6 or C_5 -C_6 fractions, C_5 -C_7 raffinate cuts from solvent extraction units which are processing catalytic reformates or pyrolysis gasoline from ethylene crackers. Paraffinic hydrocarbon feedstocks useful in the present process may be a substantially pure normal paraffin having from four to eight carbon atoms, mixtures of such substantially pure paraffins or a cycloparaffin-containing charge, i.e., cyclohexane.

The porous zeolite used herein comprises a crystalline zeolite which is a member of a class of zeolites exhibiting some unusual properties. These zeolites induce profound transformation of aliphatic hydrocarbons to aromatic hydrocarbons in commercially desirable yields and are generally highly effective in conversion reactions involving aromatic hydrocarbons. Although they have unusually low alumina contents, i.e., high silica to alumina mole ratios, they are very active even when the silica to alumina mole ratio exceeds 30. The activity is surprising since catalytic activity is generally attributed to framework aluminum atoms and cations associated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the presence of steam at high temperature which induces irreversible collapse of the framework of other zeolites, e.g., of the X and A type. An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to, and egress from the intracrystalline free space by virtue of having a pore dimension greater than about 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of silicon atoms interconnected by oxygen. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline zeolite, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra. Briefly, the preferred type zeolites useful in this invention possess, in combination: a silica to alumina mole ratio of at least about 12; and a structure providing constrained access to the intercrystalline free space.

The silica to alumina mole ratio referred to may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to alumina mole ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e., they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The type of zeolites useful in this invention freely sorb normal hexane and have a pore dimension greater than about 5 Angstroms. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the desired type. Windows of the 10-membered rings are preferred, although, in some instances, excessive puckering or pore blockage may render these zeolites ineffective. Twelve-membered rings do not generally appear to offer sufficient constraint to produce the advantageous conversions, although puckered structures exist such as TMA offretite which is a known effective zeolite. Also, structures can be conceived, due to pore blockage or other cause, that may be operative

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access, a simple determination of the "constraint index" may be made by passing continuously a mixture of an equal weight of normal hexane and 3-methylpentane over a sample of zeolite at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 1000 degrees F. for at least 15 minutes. The zeolite is then flushed with helium and the temperature adjusted between 550 degrees F. and 950 degrees F. to give an overall conversion between 10 percent and 60 percent. The mixture of hydrocarbons is passed at a 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of zeolite per hour) over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "constraint index" is calculated as follows: ##EQU1##

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeolites suitable for the present invention are those having a constraint index in the approximate range of 1 to 12. Constraint Index (CI) values for some typical zeolites are:

ZEOLITE	C.I.
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-23	9.1
ZSM-38	2
ZSM-35	4.5
Clinoptilolite	3.4
TMA Offretite	3.7
Beta	0.6
ZSM-4	0.5
H-Zeolon	0.4
REY	0.4
Amorphous Silica-Alumina	0.6 (non-zeolite)
Erionite	38

It is to be realized that the above constraint index values typically characterize the specified zeolites but that such are the cumulative result of several variables used in determination and calculation thereof. Thus, for a given zeolite depending on the temperature employed within the aforenoted range of 550 degrees F. to 950 degrees F., with accompanying conversion between 10 percent and 60 percent, the constraint index may vary within the indicated approximate range of 1 to 12. Likewise, other variables such as the crystal size of the zeolite, the presence of possible occluded contaminants and binders intimately combined with the zeolite may affect the constraint index. It will accordingly be understood by those skilled in the art that the constraint index, as utilized herein, while affording a highly useful means for characterizing the zeolites of interest is approximate, taking into consideration the manner of its determination; with probability, in some instances, of compounding variable extremes.

While the above experimental procedure will enable one to achieve the desired overall conversion of 10 to 60 percent for most catalyst samples and represents preferred conditions, it may occasionally be necessary to use somewhat more severe conditions for samples of very low activity, such as those having a very high silica to alumina mole ratio. In those instances, a temperature of up to about 1000 degrees F. and a liquid hourly space velocity of less than one, such as 0.1 or less, can be employed in order to achieve a minimum total conversion of about 10 percent.

The class of zeolites defined herein is exemplified by **ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38** and other similar materials. U.S. Pat. No. 3,702,886 describing and claiming ZSM-5 is incorporated herein by reference.

ZSM-11 is more particularly described in U.S. Pat. No. 3,709,979. the entire contents of which are incorporated here in by reference.

ZSM-12 is more particularly described in U.S. Pat. No. 3,832,449. the entire contents of which are incorporated here in by reference.

ZSM-23 is more particularly described in U.S. Pat. No. 4,076,842. the entire contents of which are incorporated herein by reference.

ZSM-35 is more particularly described in U.S. Pat. No. 4,016,245. the entire contents of which are incorporated herein by reference.

ZSM-38 is more particularly described in U.S. Pat. No. 4,046,859. the entire contents of which are incorporated herein by reference.

The specific zeolites described, when prepared in the presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 1000 degrees F. for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000 degrees F. in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this type zeolite; however, the presence of these cations does appear to favor the formation of this special type of catalyst by base exchange with ammonium salts followed by calcination in air at about 1000 degrees F. for from about 15 minutes to about 24 hours.

Natural zeolites may sometimes be converted to this type of zeolite catalyst by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite, and clinoptilolite. The preferred crystalline zeolites **are ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38**, with ZSM-5 particularly preferred.

In a preferred aspect of this invention, the zeolites hereof are selected as those having a crystal framework density, in the dry hydrogen form, of not substantially below about 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired. Therefore, the preferred zeolites of this invention are those having a constraint index, as defined above of about 1 to about 12, a silica to alumina mole ratio of at least about 12 and a dried crystal density of not less than about 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 100 cubic Angstroms, as given, e.g., on Page 19 of the article on Zeolite Structure by W. M. Meier. This paper, the entire contents of which are incorporated herein by reference, is included in "Proceedings of the Conference on Molecular Sieves, London, April 1967", published by the Society of Chemical Industry, London, 1968. When the crystal structure is unknown, the crystal framework density may be determined by classical pycnometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. This high density, of course, must be associated with a relative small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important as the locus of catalytic activity.

Crystal framework densities of some typical zeolites are:

Zeolite Void Volume Framework Density Ferrierite 0.28 cc/cc 1.76 g/cc Mordenite .28 1.7 ZSM-5- 11 .29 1.79 ZSM-12 -- 1.8 ZSM-23 -- 2.0 Dachiardite .32 1.72 L .32 1.61 Clinoptilolite .34 1.71 Laumontite .34 1.77 ZSM-4 (Omega) .38 1.65 Heulandite .39 1.69 P .41 1.57 Offretite .40 1.55 Levynite .40 1.54 Erionite .35 1.51 Gmelinite .44 1.46 Chabazite .47 1.45 A .5 1.3 Y .48 1.27

When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used. Thus, the original alkali metal of the zeolite or introduced hydrogen cations may be replaced by ion exchange with other suitable ions of Groups IB to VIII of the Periodic Table, including, by way of example, nickel, cadmium, copper, zinc, palladium, calcium or rare earth metals.

In practicing the desired method, it may be desirable to incorporate the above-described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays, which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in a raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the zeolites employed herein may be composited with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-berylia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix may vary widely with the zeolite content ranging from between about 1 to about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the composite.

The degree of zeolite catalyst activity for all acid catalyzed reactions can be measured and compared by means of "alpha value" (α). The alpha value reflects the relative activity of the catalyst with respect to a high activity silica-alumina cracking catalyst. To determine the alpha value as such term is used herein, n-hexane conversion is determined at a suitable temperature between about 500 degrees F. to 1000 degrees F., preferably at 1000 degrees F. Conversion is varied by variation in space velocity such that a conversion level of up to about 60 percent of n-hexane is obtained and converted to a rate constant per unit volume of zeolite and compared with that of silica-alumina catalyst which is normalized to a reference activity of 1000 degrees F. Catalytic activity of the catalysts is expressed as multiple of this standard, i.e., the silica-alumina standard. The silica-alumina reference catalyst contains about 10 weight percent $Al_2 O_3$ and the remainder SiO_2. This method of determining alpha, modified as described above, is more fully described in the "Journal of Catalysis", Vol. VI, pages 278-287, 1966, the entire contents of which are incorporated herein by reference.

One measure of comparison used to relate catalyst activities is "relative activity." Relative activity is the ratio of the activity of the catalyst after treatment over the initial activity. Thus, relative activity can be expressed as follows: ##EQU2##

The relative activity of a catalyst at the point of initial activity is therefore one since: ##EQU3##

The relative activity of a catalyst at the point of maximum enhanced activity can be expressed as follows: ##EQU4##

In order to increase the activity of members of this unique class of zeolites, said zeolites are treated with water, in liquid or gaseous form, e.g., steam, or water, or steam, produced in-situ. Non-limiting examples of steam produced in-situ include alcohol dehydration to produce olefins and steam; and hydrocarbon or coke combustion in the presence of oxygen to form carbon oxides and steam.

During treatment, the zeolite should be at least partially in the acidic form, e.g., hydrogen form. Suitable zeolitic forms also include those that are at least partially convertible to the hydrogen form under treatment conditions, e.g., the ammonium form, or alkyl ammonium form.

There exists a narrow range or band of conditions in which zeolite catalyst activity can be enhanced over the initial activity value. Deviations from this band of conditions can result in either non-enhancement of activity (too mild conditions), or alternatively, catalyst deactivation (too severe conditions). Such conditions include temperature, water partial pressure, treating time, nature of the zeolite, and the nature of the treating gas.

This range of conditions can be clearly demonstrated by a plot of relative activity versus a particular variable, e.g., water partial pressure, treating time, etc., with the other conditions being held constant. Such a plot is given by the drawings in which relative activity is plotted against water partial pressure with temperature and treating time being held constant. With increasing water partial pressure, activity is continuously enhanced above initial relative activity until a point of maximum enhanced relative activity is attained ($\alpha MA/\alpha^{\circ}$). Once maximum enhanced relative activity is achieved, the activity begins to decrease with increasing water partial pressure, ultimately back to the same activity as the initial relative activity (same activity as the untreated zeolite, i.e., initial activity). Increasing water partial pressure after this return to initial activity will eventually result in catalyst deactivation (too severe conditions).

Catalyst activation occurs in a limited region of conditions which can be defined as a "zone of enhanced activity." This zone encompasses those conditions which yield activities greater than the initial activity (α°). Thus, the zone is that area bounded by the activity of an untreated catalyst-initial activity and the activity of the catalyst when it returns to the initial activity. In terms of relative activities, the zone of enhanced activity is that area bounded by the initial relative activity ($\alpha^{\circ}/\alpha^{\circ}=1$) and the return to initial relative activity ($\alpha/\alpha^{\circ}=1$). The zone of enhanced activity embraces all conditions and combinations thereof yielding activities greater than the initial catalyst activity. One such activity in this zone is the maximum activity. An expression to approximately define this band in relation to two specific variables treating time and water partial pressure, with temperature held constant is as follows:

$$0.01(Pt)_T < (Pt) < 10(Pt)_T$$

Where

$$(Pt)_T = 2.6\times10^{-9}\, e^{16000}/T;$$

P=Water Partial Pressure, atmospheres;

t=Treating Time, hours;

T=Temperature, degrees K.

In regard to the condition of zeolite nature, two particular factors can be evaluated. One factor is the specific zeolite employed, such as **ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38,** etc. Another factor is the crystal size of the particular zeolite employed. For the purposes of this disclosure, small crystal size zeolites are those generally of 0.02 to 0.05 microns and large crystal size zeolites are those of generally 0.1 microns and greater.

The use of large crystal size zeolites rather than small crystal size zeolites has the effect of extending the zone of enhanced catalytic activity. Whereas both large and small size zeolites would conform to the above given relationship of $0.01(Pt)_T < (Pt) < 10(Pt)_T$, for only small size zeolites, the following preferred range is also applicable:

$0.01(Pt)_T < (Pt) < 1.0(Pt)_T$.

The extent of the zone of enhanced activity can also be modified by adjustments in the controlled conditions of treating time, temperature and water partial pressure. The interdependence of these variables (controlled conditions) are such that, for example, an increase in water partial pressure, at constant temperature, will lessen the required treating time to attain a certain activity enhancement. Likewise, increasing the temperature, at constant water partial pressure also lessens the required treating time to attain a specific activity enhancement.

The nature of the treating gas is another influential factor in catalyst activity enhancement. The treating gas in all cases contains either steam or steam producing compounds and mixtures. However, when ammonia is a constituent of the treating gas, even greater zeolite maximum activities than those attainable by steam alone can be achieved. Also the zone of enhanced activity is extended. The preferred range for ammonia addition is from about 0.01 to about 10 mole ratio ammonia/steam and more preferably from about 0.1 to about 1.0 mole ratio ammonia/steam.

The catalyst of this invention comprises a porous zeolite of enhanced acid activity containing a minor proportion of a Group VIII metal. Generally the amount of such metal component will be between about 0.1 and about 10 percent based on the weight of the porous tectosilicate. The Group VIII metal may be introduced from a suitable source, e.g., chloroplatinic acid, and impreganted on the porous zeolite either before or after the treatment of the zeolite resulting in the enhanced activity thereof. Alternatively, the Group VIII metal may be incorporated into the catalyst by ion exchange of a suitable Group VIII metal solution with the catalyst. Again, the acid activity of the catalyst may be enhanced either before or after the ion exchange procedure. The Group VIII metal component may also be deposited on a separate support, generally an inorganic oxide such as alumina, which supported metal is thereafter combined in particle form with the porous zeolite of enhanced acid activity. All of these methods of incorporating a Group VIII metal component into the catalyst are those conventionally used in the art and the details thereof will be apparent to those skilled in the art. It is contemplated that any Group VIII metal may be employed, i.e., iron, cobalt, nickel or metal of the platinum series. Particularly preferred are platinum and palladium.

The isomerization process described herein may operate at pressure from about atmospheric to superatmospheric. Generally, it is contemplated that the pressure utilized in the present process will be between about 0 and about 1000 psig, and preferably between about 100 and 500 psig. Temperature of the process will vary with the nature of the paraffinic charge stock. Generally, the temperature employed is within the approximate range of 200 to 900 degrees F.

The amount of hydrogen present to produce formation of branched chain isomers in accordance with the process of this invention is governed by the nature of the paraffinic hydrocarbons reacted as well as the nature of the reaction per se. In general, the molar ratio between hydrogen and the hydrocarbons may extend from about 0.1:1 to about 20:1.

4.5 Isomerization of Olefins by Alkylation and Dealkylation of Aromatic Hydrocarbons with Acidic Catalyst such as Molecular Sieves.

Description:

The present invention relates to a process for the skeletal isomerization of olefins. More particularly the process involves aromatic alkylation/dealkylation to convert linear olefins to branched olefins (also referred to herein as isoolefins or tertiary olefins) and to separate olefins from paraffins.

The skeletal isomerization of olefins is an important reaction for the fuel and chemical industries. For example, isomerization of n-butene to isobutylene and n-pentenes to isoamylenes has been practiced to produce isoolefins. Since n-pentenes have lower octane numbers than isopentenes, the n-pentene isomerization is useful for motor fuel production. The isomerization of n-butenes and n-pentenes to isoolefins used to produce oxygenates such as methyl tertiary butyl ether (MTBE) and tert-amyl methyl ether (TAME) is increasingly important for the formulation of reformulated gasoline (RFG). The ethers are used as octane improvers in gasoline and to reduce undesirable emissions.

Currently there is no simple technology to separate olefins from paraffins and convert linear olefins to branched olefins. Heretofore high purity isoolefins (primarily tertiary olefins) were primarily produced by separating tertiary olefins from the mixture of olefins using the "cold acid" process, i.e. sulfuric acid extraction, however sulfuric acid in general processes are not generally environmentally desirable nor is this process particularly cost efficient.

Conventional fixed bed straight pass isomerizations of olefins are equilibrium limited, thus limiting practically achievable yield of isoolefins. The isomerizations are carried out using acidic catalysts such as molecular sieves and the like.

Temperature favorable

Skeletal isomerization has been carried out with acidic catalysts such as fluorinated alumina, SAPO (silicoaluminophosphates), ALPO (aluminophosphates), ferrierite, aluminosilicates, zeolites, clays, etc. It has been known that ferrierite and ZSM-35 are shape selective zeolite catalysts for n-butene skeletal isomerization to isobutylene. The most preferred mode of carrying out the isomerization is the vapor phase fixed bed operation, in which a tubular reactor is packed with heterogeneous acidic catalysts and the vapors of the olefinic hydrocarbon feed stocks are passed through the catalyst bed at the temperatures which are effective for the skeletal isomerization. Usually the double bond isomerization of olefins is much easier than the skeletal isomerization and hence the temperatures required for the double bond isomerization are much lower than the skeletal isomerization temperatures.

The skeletal alteration of alkyl groups of alkyl aromatic compounds such as butyl group of butylbenzene is another kind of isomerization which is different from olefin isomerization. R. M. Roberts et al (JACS Vol 81, 640, 1959) explained the structural isomerization between sec-butyl and isobutyl groups without breaking the butyl group from the benzene ring. The interconversion among sec-butylbenzene, isobutylbenzene and tert-butylbenzene is demonstrated by acid catalyzed reaction.

Composition

The composition of the equilibrium mixture contains only a small amount of tert-butylbenzene, probably due to high instability of the tert-butylbenzene carbonium ion. The isomerization of butyl groups proceeds throughout the formation of a couple of intermediates, a .sigma.-bonded complex intermediate first formed by the interaction of alkylaromatic compounds with an acidic site on a catalyst and then converted to a methyl-bridged .pi.-complex intermediate.

Regenaration of catalyst

The catalyst used in the conventional process for skeletal isomerization of olefins generally suffers relatively fast catalyst deactivation caused by deposition of heavy carbonaceous materials (coke) on the catalyst surface and pores. Therefore, there is always fast initial catalyst deactivation regardless of catalysts. Because of this fast initial catalyst deactivation and other competing reactions, the skeletal isomerization becomes impractical at the temperatures below about 350.degree. C. Since the olefinic hydrocarbon feed stocks usually contain a small amount of dienes and alkynes in addition to olefins, the catalyst deactivation becomes even faster. Therefore, frequent catalyst regeneration is necessary. To overcome slower isomerization reaction rates, the reaction temperature has to be raised. This can lead to even faster catalyst deactivation and often increases the cracking reactions, producing lighter products than intended.

Therefore, the catalyst regeneration or the replacement of deactivated catalyst with a fresh catalyst becomes necessary. In fact, often the catalyst regeneration cycle length is one of the major determining factors whether a process becomes commercially successful or not. Aromatic alkylation with olefins is widely practiced to produce various alkylated products and can be achieved with various acidic catalysts. Zeolite catalysts are known to be among the best for this purpose.

Dealkylation

Dealkylation is carried out vapor phase dealkylation of tert butyl aromatic compounds such as tert-butylbenzene, p-tertiary butyltoluene and p-tert butyl ethylbenzene over a silica-alumina catalyst. Tert-butyltoluene was dealkylated over a Y-zeolite catalyst. The dealkylation reactivities of three butylbenzene isomers over silica-alumina catalysts were investigated by P. Andreu et al (J of Catalysis, Vol. 21, 225, 1971). The reactivity decreases in order of tert-, sec- and n-butylbenzene. The dealkylation of tert-butylbenzene at 180.degree. to 360.degree. C. produced only isobutylene as olefin product.

Mechanism of dealkylation

Two different mechanisms are proposed for the dealkylation of sec-butylbenzene; one for the temperatures lower than 400.degree. C. and the other for the temperatures higher than 400.degree. C. The olefin products of dealkylation at temperatures below 400.degree. C. contain little isobutylene. The acid catalyzed dealkylation of alkylbenzene compounds such as toluene, ethylbenzene, isopropylbenzene and tert-butylbenzene. The dealkylation of alkylaromatic compounds is suggested to occur through the sequential formation of two intermediates. The first intermediate (charge delocalized phenyl cation) is formed by protonation of the benzene ring of alkylaromatic compounds. This intermediate decomposes to benzene, and the alkyl carbonium ion (the second intermediate). This second intermediate decomposes to olefin product with or without the skeletal isomerization.

The present invention provides a method of separating olefins from paraffins. An advantage of the present process is that the dealkylation of the alkylated aromatic product provides a desired mixture of olefin isomers which are easily separated from the aromatic compounds. This advantage arises from the substantial difference in boiling point between the olefins and the aromatics.

No art is known which discloses the skeletal isomerization of olefins by the alkylation and dealkylation of aromatic compounds therewith. The reaction of olefins with aromatic compounds in the presence of paraffins, separation of the alkylated material, dealkylation of the alkylated material and recovery of skeletally isomerized olefins is not disclosed in the art.

SUMMARY OF THE INVENTION:

Broadly, the invention is an olefin skeletal isomerization process for C.sub.4 to C.sub.15 olefins by the reaction of at least one C.sub.4 to C.sub.15 olefin, having a first skeletal distribution, with aromatic compounds under alkylation conditions to produce an alkylated aromatic product, dealkylation of the alkylated aromatic product under dealkylation conditions to produce a dealkylated product comprising said aromatic compounds and olefins corresponding to the olefins in the alkylation and having a second skeletal distribution different than said first skeletal distribution. The olefins fed to the alkylation are isomerized during the alkylation/dealkylation.

The **term "skeletal distribution" means** the relative composition of the branched to linear isomers of a given olefin. For example, a C.sub.4 feed to the alkylation reaction may contain only butene-1 and butene-2, thus its skeletal distribution is o % branched olefins and 100% linear olefins and after the dealkylation there is 50% tert-butylene and the balance butene-1 and butene-2, thus the skeletal distribution of the dealkylated olefins is 50% branched and 50% linear.

The alkylation reaction is preferably carried out under conditions to achieve substantially 100% conversion of the olefins present. Since the olefins are usually present as part of an aliphatic stream, containing paraffins and olefins, the alkylation serves to also separate the alkenes from the remainder of the stream. During the alkylation step, the alkylated aromatic compounds may contain both branched and linear alkyl groups due to the skeletal rearrangement of alkyl groups depending on the alkylation temperature even if only linear olefins are present in the feed.

Acidic **catalysts are employed in both the alkylation and the dealkylation** steps. **Molecular sieves are preferred catalysts for both reactions and zeolites more preferred.**

The aromatic compounds from the dealkylation may be recovered and recycled to the alkylation unit to repeat the process. Similarly linear olefins may be recovered and recycled to either the alkylation reaction or dealkylation reaction. One method of recovering the tert-olefins which comprise a part of isoolefins and to separate said tert-olefins from the olefin mixture is to contact the mixture of olefins with a C.sub.1 to C.sub.8 alcohol to selectively react the tert-olefins to form ethers as described hereinabove. The unreacted olefins from this reaction are easily separated from the ethers for recycle to the alkylation reaction or otherwise employed.

The alkylation and dealkylation reactions may either one or both be carried out in straight pass fixed beds or in catalytic distillation reactors using suitable acidic catalysts such as Al containing materials e.g. alumina and molecular sieves including zeolites. The dealkylation of the alkylate may be carried out using the same or similar catalyst to the alkylation, i.e. acidic catalyst, such as a zeolite. The dealkylation conditions are more severe than the alkylation conditions but in both reactions there may be some reverse reaction. Hence, the reactions carried on by catalytic distillation are advantageous because the reaction products are concurrently separated from the inerts and the distillation can be operated to hold the reactant feed within the catalytic distillation structure bed (in the case of the alkylation the aromatic is maintained in the catalyst zone and the alkylated product removed and in the case of the dealkylation the alkylate product is held in the catalyst zone and the aromatic and olefins removed).

In one embodiment the aromatic alkylation reaction is carried out in a catalytic distillation reactor using a feed that contains paraffins, linear olefins and/or branched olefins using zeolite catalyst wherein a portion of the olefins, up to about 100% conversion of olefins to alkyl aromatics whereby the paraffins and a portion of the excess aromatics are separated from the alkylated products by distillation within the distillation reactor. The separated mixture composed of the alkylated aromatic products and a portion of aromatics is passed through a fixed bed catalytic dealkylation reactor to produce branched olefins. The branched olefin content in the olefin product has been found to equal or higher than that in a conventional olefin isomerization.

In another embodiment the dealkylation of a tert-alkyl aromatic compound is carried out in a catalytic fixed bed reactor. When the dealkylation temperature is relatively low, the olefin product is mostly composed of branched olefin, indicating that there is little isomerization of branched olefin to linear olefin or skeletal rearrangement of tert-alkyl group of the starting alkyl aromatic compound to linear alkyl group. However, as the dealkylation temperature is raised, the linear olefin content in the olefin product was increased steadily, indicating the increased skeletal isomerization of tert-olefin to linear olefin as well as the skeletal isomerization of tert-alkyl group to linear alkyl group.

Undealkylated material is preferably separated from the olefins and returned to the dealkylation zone and the aromatics separated from the olefins and returned to the alkylation zone.

DETAILED DESCRIPTION

Reactants

The olefins are preferably C.sub.4 to C.sub.10 olefins, more preferably C.sub.4 to C.sub.8 olefins, including normal and iso forms thereof. For example, suitable olefins are butenes, isobutene, 1-pentene, 1-hexene, 2-hexene, 2,3-dimethyl-1-pentene, 1-octene, 1-nonene and 1-decene, dodecene and the like. As described above a special case uses a feed, high in linear olefins which are isomerized during the process to the corresponding iso forms.

The aromatic compounds are preferably organic aromatic compounds under the pressure conditions of the distillation column reactor. The organic aromatic compounds include hydrocarbons of one or more rings and 6 to 20 carbon atoms which may contain substituents which do not interfere with the alkylation including halogen (Cl, Br, F and I), OH and alkyl, cycloalkyl, aralkyl and alkaryl groups of 1 to 10 carbon atoms. Suitable organic aromatic compounds include benzene, xylene, toluene, phenol, cresol, ethyl benzene, diethyl benzene, naphthalene, indene, phenyl bromide, 1,2-dihydronaphthalene and the like, a preferred group of compounds for use in the present process is benzene, xylene, toluene, phenol, and cresol. A preferred group of compounds for use in the present process is benzene, xylene and toluene. Mixtures of aromatic compounds and mixtures of olefins can be used as the feeds for the present process, as may relatively pure streams of either or both.

Alkylation

In the alkylation the mole ratio of organic aromatic compound to olefin may be in the range of 1:1 to 100:1, preferably 2:1 to 50:1 and more desirably about 2:1 to 10:1.
The alkylation reaction is carried out in the presence of acidic catalysts. The preferred catalysts are zeolite Beta, Y-zeolite, ferrierite, mordenite, ZSM-5, ZSM-11, supported phosphoric acid (SPA), acidic resin, etc.

Dealkylation

The dealkylation of alkylated products may be carried out in the presence of acidic catalysts. The preferred catalysts are molecular sieves, purified acidic natural clays and amorphous alumino-silicates. The preferred molecular sieve catalysts are one, two, or three dimensional medium to large pore size (from 3.50 to 7.6 A.degree., preferentially from 3.5 to 7.5 A.degree.) sieves such as ferrierite, SAPO-11, SAPO-35, ZSM-5, ZSM-22, ZSM-23, ZSM-57, zeolite beta, pentasil zeolite and zeolite Y.
The dealkylation may be carried out in vapor phase or in the presence of both vapor and liquid by employing both fixed bed and catalytic distillation column reactors. The feeds to the dealkylation reactor can be pure alkylates or mixtures of alkylates and aromatic compounds such as benzene, toluene and xylene or paraffins. Since the dealkylation reaction is endothermic reaction, diluted alkylate is desirable to achieve high conversion unless a multiple reactor system is employed with intermittent reheating or more complex reactors such as tube or sheet plate heat exchanged reactors. The products of dealkylation are olefins and aromatics. The olefin products from the dealkylation are composed of the olefin isomers from which tert-olefins may be selectively reacted with alcohols, water, carboxylic acids or aromatic compounds. The remaining linear olefins are returned to either the alkylation reactor or dealkylation reactor to convert to tert-olefins.

The range of temperature for the dealkylation is from 180.degree. to 550.degree. C., preferably from 200.degree. to 450.degree. C. In general, lower pressure is favored for the dealkylation reaction. The range of pressure is from subambient to 350 psig, preferably from ambient to 150 psig.

The alkyl aromatic compound can be pure or mixtures with various aromatic or paraffinic compounds. Depending on the components in the mixtures of alkyl aromatic compounds, the selection of catalyst and operating conditions, the olefin products are pure or substantially pure tert-olefins, substantially pure linear olefins or mixtures of olefin isomers.

The present alkylation reaction can be carried out from ambient pressure to high pressure, e.g., 1 to 40 atmospheres. In the reactor distillation column the temperature will vary depending on the local composition, i.e., the composition at any given point along the column. Furthermore, the temperature along the column will be as in any distillation column, the highest temperature will be in the bottom and the temperature along the column will be the boiling point of the compositions at that point in the column under the particular conditions of pressure. Moreover, the exothermic heat of reaction does not change the temperature in the column, but merely causes more boil up. However, the temperatures within the column with the above considerations in mind will generally be in the range of 50.degree. C. to critical temperature of the mixture, preferably 70degreeC. to 300degree. C. at pressures of 1 to 20 atmospheres

If the feed for the dealkylation is composed of various alkyl aromatic compounds whose alkyl groups are composed of tert, sec, iso and n-alkyl groups, the dealkylation can be carried out selectively or nonselectively, depending on the purpose of dealkylation or the application of olefin products. For a given catalyst, lower temperatures are employed for the selective dealkylation of tert-alkyl aromatic compounds to tert-olefins. On the other hand, higher temperatures are employed for the nonselective dealkylation to produce the mixed olefin products containing various olefin isomers. For example, if a part of alkyl aromatic compounds are composed of tert-alkyl group containing compounds, pure or substantially pure tert-olefins can be produced by carrying out the dealkylation at lower temperature. It is important that the dealkylation is not carried out at too high temperatures because the olefin product will contain linear olefins due to the skeletal rearrangement of some of the tert-olefin products or tert-alkyl group of alkyl aromatic compounds. The dealkylation of the remaining unconverted alkyl aromatic compounds at higher temperatures produces mixed olefin product of olefin isomers whose composition is near equilibrium distribution. The optimum temperatures for dealkylation depends on the alkyl group on the alkylate and the catalyst employed. For example, when ferrierite molecular sieve is employed as catalyst for the dealkylation of tert-butyl toluene, it is desired to carry out the dealkylation at temperatures lower than about 570.degree. F. For a given acid catalyst, tert-alkyl aromatic compound can be dealkylated at temperatures lower than the corresponding sec-alkyl aromatic compounds. Tert-alkyl aromatic compounds can be dealkylated over mildly acidic catalysts.

The works of R. M. Roberts and D. Farcasiu discussed above may suggest a reaction mechanisms involved in the conversion of linear olefins to isoolefins via the consecutive alkylation-dealkylation reactions disclosed in this invention. These consecutive reactions can be carried out in one step or two steps. If the alkylation is carried out at higher temperatures and low pressures, both alkylation and dealkylation as well as olefin isomerization can occur simultaneously in the catalytic reaction zone, resulting in the olefin isomers in the reaction products in one step. However, if the alkylation reaction is carried out at lower temperature and high pressure, and the dealkylation is carried out at higher temperature and lower pressure, the same result can be obtained in two steps.

The products from the dealkylation step are mixtures of isoolefins and linear olefins from which isoolefins (branched olefins) can be separated from linear olefins by existing technologies such as extractive distillation or selective reaction such as etherification. In the selective reaction technique, the separation of isoolefins in the mixtures is achieved by reacting isoolefins with a number of reactants. Since isoolefins are much more reactive than linear olefins, isoolefins in the mixtures can be reacted selectively with alcohols, water, carboxylic acids and aromatics, and then unreacted linear olefins are separated from higher boiling reaction products by simple distillation technique. The recovered linear olefins are recycled back to the alkylation reactor.

When alcohol such as methanol or ethanol is employed for the selective reaction agent for isoolefins, ether such as methyl tert-butyl ether or ethyl tert-butyl ether is the reaction product. These ethers are valuable products, for these ethers have been used for the blending components as oxygenates and octane component for the reformulated gasoline. If isoolefins are desired products, these ethers are dealkylated to isoolefins and alcohols, and isoolefins are separated from alcohols by simple distillation. Therefore, this invention provides a means to convert low RON olefin components in the mixtures to high RON as well as lower high vapor pressure components in gasoline. It is desirable to reduce the olefin and aromatic components in the gasoline due to environmental and other reasons. Ethers are excellent replacement components for this purpose. Therefore, this invention provides a useful technology for the production of MTBE or TAME from the mixed olefin streams.

When aromatic compounds such as benzene, toluene, xylenes or phenols are employed for the selective reaction agents with isoolefins, tert-alkyl aromatic compounds are reaction products. When isoolefins are desired products, these tert-alkyl aromatic compounds are dealkylated in the presence of acidic catalysts. It is important that the dealkylation is not carried out at too high temperatures. If the dealkylation temperature is too high, the olefin product will contain linear olefins.

If the alkyl groups of alkyl aromatic compounds are composed of linear alkyl groups and linear olefins are desired products, the dealkylation is carried out at lowest possible temperature by employing less acidic catalysts.

Straight pass Reactor

For the fixed bed straight pass alkylation, the olefin and aromatic feeds are premixed prior to entering the catalytic reaction zone. Another technique carrying out this fixed bed alkylation is that olefin feed is divided into several portions and then each portion is fed to the alkylation reactor at the different locations as the aromatic feed flows through the fixed bed reactor. For this fixed bed operation, the reactor effluent stream may be recycled to improve the selectivity and dilute the heat of reaction, because the alkylation reaction is exothermic. The preferred range of the temperature for the alkylation is from 50.degree. to 500.degree. C., preferably from 80.degree. to 300.degree. C. The pressure for the alkylation reactor should be high enough so that a portion of aromatics would exist as liquid form. Therefore, the pressure for the alkylation reactor depends on the temperature and the composition of the feed to the reactor.

Distillation Column Reactor

When the alkylation is carried out by employing the catalytic distillation reactor, a distillation column is loaded with acidic catalysts, and light olefins such as C.sub.4 or C.sub.5 olefins may be introduced into the distillation tower at the bottom section of tower and aromatics such as toluene or xylene may be introduced into the distillation tower at the top section of the tower, or both olefins and aromatics are introduced at the lower section of the tower depending on the operating condition such as temperature and pressure required for the effective alkylation and separation of paraffins from aromatics or aromatics from the alkylated products. Unreacted paraffins in the olefin containing feed are separated from the reaction mixture as overhead product, and the alkylates (alkylated products) and possibly some of the aromatics are withdrawn at the bottom of the tower as the bottom product. If desired, one may remove a part of the aromatics as the overhead product along with paraffins.

After the dealkylation of alkylate is carried out, the products, olefins and aromatics, are removed from the column as overhead, and unreacted alkylates are recovered as the bottom product to recycle back to the top of the catalyst. The desired conversion per pass is from 10 to 100%, preferentially 30 to 80%.

When the dealkylation is carried out by employing the catalytic distillation column reactor, the column pressure should be high enough so that, at least, a part of feed would exist in liquid form. The product olefins are removed from the catalytic reaction zone as the overhead product. The unconverted alkylates are removed from the bottom of the column and recycled to the top of the catalyst.

When alkylation is carried out in the catalytic distillation mode, the exact location of the olefin feed in the distillation column reactor will depend on the particular feeds and the desired product. In one embodiment the olefin feed to the reactor is preferably made below the catalyst bed thereby allowing mixing of the reactants before contact with the catalyst bed. In another embodiment the olefin feed to the reactor is preferably made above the catalyst bed.

The aromatic feed may be added at any point in the distillation column reactor, however, preferably it is added below the fixed bed or to the reflux as makeup, depend on its boiling point. Preferably there is a large excess of the aromatic to the olefin in the reactor in the range of 2 to 100 moles of aromatic per mole of olefin, that is the net molar feed ratio of aromatic compound to olefin may be close to 1:1, although the catalytic distillation system is operated so as to maintain a substantial molar excess of aromatic compound to olefin in the reaction zone. The alkylated product is the highest boiling material and is separated in the lower portion of the column usually as bottoms. The organic aromatic compound can be the second highest boiling or third highest boiling component.

Very large molar excesses of aromatic compounds require a very high reflux ratio in the column, and a low unit productivity. Hence, the correct ratio of aromatic compound to olefin must be determined for each combination of reactants as well the acceptable olefin content in either the overhead or alkylation product.

The length of the catalyst bed in the column, particularly that portion wherein the reactants are in contact and the reaction occurs, depends on the reactants, location of the olefin feed and the acceptable unreacted olefin in the streams leaving the tower. Some degree of testing will be required for each set of reactants and parameters of stream purity following present disclosures.

The advantages of present alkylation carried out in the catalytic distillation mode are derived from the continuous wash-off of the coke or coke precursors on the catalyst surface, resulting in much longer catalyst life, the natural separation of products in the catalytic reaction zone, the steadier flow of the reactants to the catalytic reaction zone, better transport of materials between the bulk phase and the reaction zone, and better temperature control caused by dynamic vapor-liquid equilibrium and vapor traffic then the traditional fixed bed process.

The alkylate products are composed of a number of different alkyl groups. For example, when n-butenes are olefins for the alkylation, the alkyl groups on the alkylated aromatic compounds are mostly sec-butyl and tert-butyl groups. The degree of isomerization of alkyl group depends on the temperature. For example, if the alkylation is carried out at temperatures lower than about 400.degree. F. with molecular sieve catalysts, then alkylation products contain a small amount of tert-butyl aromatic compounds. When n-pentenes are used, the alkyl groups are isomers of C.sub.5 such as sec-pentyl, 3-methyl-butyl, tert-amyl, etc. If a mixed C.sub.5 stream such as TAME raffinate is used for the alkylation, the paraffin components in the mixed feed can easily be separated from the alkylate and can serve as feed stock for the steam cracker for the ethylene production or the paraffin skeletal isomerization, because it contains little or no olefins.

In some reactions in the distillation column reactor, the olefin will be a higher boiling material than the aromatic hydrocarbon, e.g., C.sub.8 + olefins. In such instances in a catalytic distillation reaction any unreacted olefin will appear in the bottoms alkylation product, although a side draw may be used to reduce such material in the product to an insignificant level. However, operating the reaction with far less than a stoichiometric amount of olefin in the reaction zone, as described, will normally keep the olefin level in the bottoms low or entirely eliminated.

Catalyst

The particulate molecular sieves or other catalysts may be employed by enclosing them in a porous container such as cloth, screen wire or polymeric mesh for use in catalytic distillation. The material used to make the container must be inert to the reactants and conditions in the reaction system. The cloth may be any material which meets this requirement such as cotton, fiber glass, polyester, nylon and the like. The screen wire may be aluminum, steel, stainless steel and the like. The polymer mesh may be nylon, teflon or the like. The mesh or threads per inch of the material used to make the container is such that the catalyst is retained therein and will not pass through the openings in the material. Particles of about 0.15 mm size or powders may be used and particles up to about 1/4 inch diameter may be employed in the containers.

The container employed to hold the catalyst particles may have any configuration, such as the pockets disclosed in the commonly assigned patents above or the container may be a single cylinder, sphere, doughnut, cube, tube or the like.

Each container containing a solid catalytic material comprises a catalyst component. Each catalyst component is intimately associated with a spacing component which is comprised of at least 70 volume % open space up to about 95 volume % open space. This component may be rigid or resilient or a combination thereof. The combination of catalyst component and spacing component form the catalytic distillation structure. The total volume of open space for the catalytic distillation structure should be at least 10 volume % and preferably at least 20 volume % up to about 65 volume %. Thus desirably the spacing component or material should comprise about 30 volume % of the catalytic distillation structure, preferably about 30 volume % to 70 volume %. One suitable spacing material is open mesh knitted stainless wire, known generally as demister wire or an expanded aluminum. Other resilient components may be similar open mesh knitted polymeric filaments of nylon, teflon and the like. Other materials such as highly open structures foamed material, e.g., ceramic or metal foam monolith structures (rigid or resilient) may be formed in place or applied around the catalyst component. In the case of larger catalyst components such as from about 1/4 inch to 1/2 pellets, spheres, pills and the like, each such larger component may be individually intimately associated with or surrounded by the spacing component as described above. It is not essential that the spacing component, entirely cover the catalyst component. It is only necessary that the spacing component intimately associated with the catalyst component will act to space the various catalyst components away from one another as described above. Thus, the spacing component provides in effect a matrix of substantially open space in which the catalyst components are randomly but substantially evenly distributed.

One catalytic distillation structure for use herein comprises placing the molecular sieve particles into a plurality of pockets in a cloth belt, which is supported in the distillation column reactor by open mesh knitted stainless steel wire by twisting the two together in a helical form. This allows the requisite flows and prevents loss of catalysts. The cloth may be any material which is inert in the reaction. Cotton or linen is useful, but fiber glass cloth is preferred.

The lower portion of the column is a conventional distillation column configuration. Make-up benzene is conveniently added via line 14. The olefin containing feed 8 is mixed with the benzene and fed to the column via 9 just below the catalyst packing 12 for better mixing. The reaction is exothermic and initiated by contacting the two reactants in the catalyst packing. The alkylated products are higher boiling than benzene and the C.sub.4 feed, and are recovered via 18 as a bottoms product. The feed of C.sub.4 's is adjusted such that there is a molar excess of benzene in the reactor. In addition to the C.sub.4 alkanes and benzene and other lights go off as overhead 20. The overhead is passed to condenser 22 which is operated to condense substantially all of the benzene which passes via 24 to accumulator 16 and hence, by reflux via 26 to column 10. The benzene used in the reaction and lost with the lights, primarily C.sub.4 alkanes (which exit accumulator 16 via 28) is made up by fresh benzene feed 14.

The bottoms contain a mixture of isobutene alkylated benzene and primary and secondary butyl benzene which passes via 18 to dealkylation unit 30, which is a catalytic distillation column operated to concurrently dealkylate the alkylate and fractionate benzene and butenes as overhead 32 and the heavies as a bottoms product 33. In this embodiment the benzene is separated from the olefin in column 35 and returned via 34 to the feed 14 to column 10. The olefins are recovered as overheads 36.

The lower portion of the column is a conventional distillation column configuration. Make-up toluene is conveniently added via line 114. The olefin containing feed 108 is mixed with the toluene recycle 154 and the non isoolefin recycle 162 and fed to the column via 109 below the catalyst packing 112 for better mixing. The reaction is exothermic and initiated by contacting the two reactants in the catalyst packing. The alkylated products are higher boiling than toluene and the C.sub.4 or C.sub.5 feed and are recovered via 118 as a bottoms product. The feed of C.sub.4 or C.sub.5 is adjusted such that there is a molar excess of toluene to olefin in the reactor. In addition to the C.sub.4 or C.sub.5 alkanes, other lights and some toluene go off as overhead 120. The overhead 120 is passed to a condenser (not shown) to condense substantially all of the toluene which is returned to column 110 as reflux.

The bottoms in column 110 contain a mixture of alkylated toluene (the olefins are substantially 100% converted) which pass via 118 to dealkylation unit 130, which is a fixed bed straight pass reactor operated to concurrently dealkylate the toluene alkylate. The total dealkylation product is passed via line 132 to distillation column 140 where the undealkylated material is separated and recycled via line 144 to the dealkylator 130. The toluene and olefins are recovered as overhead via line 142 to distillation column 150, where the aromatic are recovered as a bottoms via line 154 and recycled to the alkylation column 110. In this embodiment the olefins are passed to an ether plant 160 where the isoolefins are preferentially reacted with alcohol, such as methanol to form MTBE or TAME. Make up olefin feed may be added via line 156. The ether plant may be any of those known in the art. The present system has a double benefit when used in conjunction with an ether plant. First because there is a conversion of linear olefins to isoolefins the efficiency of the ether unit is increased, two ways, first by conversion of the linear olefins in the make-up feed and conversion of the recycled linear olefins from the ether plant to the present system. The second benefit is the removal of potential poisons for the etherification catalyst.

Conclusion

It is well known that the more highly branched isomers of the paraffinic hydrocarbons occurring in petroleum gasoline fractions are more valuable than the corresponding slightly branched or straight chain hydrocarbons because of their higher octane ratings. The demand for motor fuels of greater octane number has increased markedly as the automotive industry has provided gasoline engines with increasingly higher compression ratios to attain greater efficiency.

Isomerization of paraffins larger than C_6 is one way to improve octane without increasing the aromatic or olefin content. n-C_7 has a research octane rating of 0, while 2-methyl hexane and 2,3-dimethyl pentane have research octane ratings of 53 and 93, respectively. C_7 paraffins are relatively abundant in naphtha, and their isomerization is a natural extension to existing C_5/C_6 isomerization.

Discovery of a suitable technology and catalysts which could convert the especially the n-parafins in C_7+ range (having RONC < 17) into isomers having 90+ RONC without cracking the hydrocarbons would be a boon to refiners and provide eco-friendly gasoline by minimizing olefines and aromatics.

Abundant availability of light naphtha (90-140°C cut) that mainly contains C_7+ hydrocarbons is a great source for the isomerization reaction.

In this project ,we have done the comparative study of different acidic catalyst used for the isomerization.we have studied about the special(unique) properties of the catalyst,their feed composition ,feed conditions,reaction conditions like temperature, pressure,mole ratios of the reactants; mole ratio of the elements used as a catalyst,reaction time etc.

For example we have studied the behavior of one of the acidic catalyst-**triflouromethane sulfonic acid**

1. **Catalyst used:** triflourosulfonic acid or triflourosulfonic acid and a groupn of Vb metaln fluoride.specific example of these metal fluorides are antimony pentaflouride,arsenic pentaflouride
2. **Speciality of the catalyst used:**

- It has a much higher boiling point hence less is lost on recycle in continuous operation.
- It does not attack glass so sight gages etc made of glass can be used.
- It is the strongest protonic acid known and hence smaller amounts of acid are effective.

3. **Feed composition:** normal and branched chain paraffinic hydrocarbons having from 4-7 carbon atom/molecule

4. **Reaction conditions for isomerization of the feed :**

Temperature: 0-100^{0}C

Usually 15 to 80 ^{0}C

Pressure: sufficient to maintain the hydrocarbon reactants and catalysts as liuid in reaction zone.

5. **Reaction time:** in general reaction times ranging from about 5 minutes to 48 hrs.

Preferably 15 minutes to 2 hrs are employed.

6. **Mole ratio of paraffinic hydrocarbon to groupVb metal fluoride forming the catalyst:**

50:1 to 0.2:1

Preferably1:1 to 20:1

Process is conducted as a batch or a continuous operation.

The other studied catalysts are mordenite catalyst,zeolite with high steam enchanced acidity catalyst and the acidic catalyst used for the alkylation and dealkylation of aromatic hydrocarbons such as molecular sieves.

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