ISOMERIZATION CATALYST AND PROCESSES

BACKGROUND OF THE INVENTION

[0001] This invention relates to an improved catalytic composite and process for the conversion of hydrocarbons, and more specifically for the selective upgrading of a paraffinic feedstock by isomerization.

[0002] The widespread removal of lead antiknock additive from gasoline and the rising fuel-quality demands of high-performance internal-combustion engines have compelled petroleum refiners to install new and modified processes for increased "octane," or knock resistance, in the gasoline pool. Refiners have relied on a variety of options to upgrade the gasoline pool, including higher-severity catalytic reforming, higher FCC (fluid catalytic cracking) gasoline octane, isomerization of light naphtha and the use of oxygenated compounds. Such key options as increased reforming severity and higher FCC gasoline octane result in a higher aromatics content of the gasoline pool at the expense of low-octane heavy paraffins.

[0003] Refiners are also faced with supplying reformulated gasoline to meet tightened automotive emission standards. Reformulated gasoline differs from the traditional product in having a lower vapor pressure, lower final boiling point, increased content of oxygenates, and lower content of olefins, benzene and aromatics. Benzene content generally is being restricted to 1% or lower, and is limited to 0.8% in U.S. reformulated gasoline. Gasoline aromatics content is likely to be lowered, particularly as distillation end points (usually characterized as the 90% distillation temperature) are lowered, since the high-boiling portion of the gasoline which thereby would be eliminated usually is an aromatics concentrate. Since aromatics have been the principal source of increased gasoline octanes during the recent lead-reduction program, severe restriction of the benzene/aromatics content and high-boiling portion will present refiners with processing problems. These problems have been addressed through such technology as isomerization of light naphtha to increase its octane number, isomerization of butanes as alkylation feedstock, and generation of additional light olefins as feedstock for alkylation and production of oxygenates using FCC and dehydrogenation. This issue often has been addressed by raising the cut point between light and heavy naphtha, increasing the relative quantity of naphtha to an isomerization unit.

[0004] Additionally, instead of reforming, the isomerization of longer chain hydrocarbons such as C_7 and C_8 hydrocarbons into branched hydrocarbons of higher octane could be used to

increase the octane number of fuels without increasing the amount of aromatics. However, many isomerization catalysts suffer significant disadvantages when applied to the longer chain hydrocarbons. A principal problem is the generation of byproducts such as cracked hydrocarbon materials. The cracking decreases the amount of long chain paraffins available for isomerization and reduces the ultimate yield.

[0005] Several catalysts for isomerization are known, and a family of tungstated zirconia catalysts have been used. For example, US 5,510,309 B1, US 5,780,382 B1, US 5,854,170, and US 6,124,232 B1 teach methods of making an acidic solid having a Group IVB (IUPAC 4) metal oxide modified with an oxyanion of a Group VIB (IUPAC 6) metal such as zirconia modified with tungstate. US 6,184,430 B1 teaches a method of cracking a feedstock by contacting the feedstock with a metal-promoted anion modified metal oxide catalyst where the metal oxide is one or more of ZrO_2, HfO_2, TiO_2 and SnO_2, the modifier is one or more of SO_4 and WO_3, and the metal is one or more of Pt, Ni, Pd, Rh, Ir, Ru, Mn, and Fe.

[0006] Others have added a noble metal such as platinum to the tungstated zirconia catalysts above, see US 5,719,097; US 6,080,904 B1; and US 6,118,036 B1. A catalyst having an oxide of a Group IVB (IUPAC 4) metal modified with an anion or oxyanion of a Group VIB (IUPAC 6) metal and a Group IB (IUPAC 11) metal or metal oxide is disclosed in US 5,902,767. In US 5,648,589 and US 5,422,327, a catalyst having a Group VIII (IUPAC 8, 9, and 10) metal and a zirconia support impregnated with silica and tungsten oxide and a process of isomerization using the catalyst is disclosed. A process for forming a diesel fuel blending component uses an acidic solid catalyst having a Group IVB (IUPAC 4) metal oxide modified with an oxyanion of Group VIB (IUPAC 6) metal and iron or manganese in US 5,780,703 B1.

[0007] US 5,310,868 and US 5,214,017 teach catalyst compositions containing sulfated and calcined mixtures of (1) a support containing an oxide or hydroxide of IUPAC 4 (Ti, Zr, Hf), (2) an oxide or hydroxide of IUPAC 6 (Cr, Mo, W); IUPAC 7 (Mn, Tc, Re), or IUPAC 8, 9, and 10 (Group VIII) metal, (3) an oxide or hydroxide of IUPAC 11 (Cu, Ag, Au), IUPAC 12 (Zn, Cd, Hg), IUPAC 3 (Sc, Y) , IUPAC 13 (B, Al, Ga, In, Tl), IUPAC 14 (Ge, Sn, Pb), IUPAC 5 (V, Nb, Ta), or IUPAC 6 (Cr, Mo, W), and (4) a metal of the lanthanide series.

[0008] Applicant has developed a more effective catalyst that has proved to be surprisingly superior to those already known for the isomerization of hydrocarbons and especially C_7 and C_8 hydrocarbons.

SUMMARY OF THE INVENTION

[0009] The present invention is an improved catalyst and process for hydrocarbon conversion reactions. The invention also provides improved technology to upgrade naphtha to gasoline and more specifically an improved catalyst and process for the isomerization of full boiling point range naphtha to obtain a high-octane gasoline component. This invention is based on the discovery that a catalyst containing lanthanide series and platinum-group components provides superior performance and stability in the isomerization of full boiling point range naphtha to increase its isoparaffin content.

[0010] The invention is a catalyst comprising a tungstated support of an oxide or hydroxide of a Group IVB (IUPAC 4) metal, preferably zirconium oxide or hydroxide, at least a first component which is a lanthanide series element and/or yttrium component, and at least a second component being a platinum-group metal component. The first component preferably consists of a single lanthanide-series element or yttrium and the second component preferably consists of a single platinum-group metal. Preferably, the first component is ytterbium, holmium, yttrium, cerium, europium, or mixtures thereof, and the second component is platinum. The catalyst optionally contains an inorganic-oxide binder, especially alumina. One method of preparing the catalyst of the invention is by tungstating or tungstating and the Group IVB (IUPAC 4) metal oxide or hydroxide, incorporating a first component which is at least one lanthanide element, yttrium, or any mixture thereof, and the second component which is a platinum-group metal, and preferably binding the catalyst with a refractory inorganic oxide.

[0011] The catalyst of the invention may be used for converting hydrocarbons such as in the isomerization of isomerizable hydrocarbons. The hydrocarbons preferably comprise a full boiling point range naphtha which is isomerized to increase its isoparaffin content and octane number as a gasoline blending stock.

[0012] These as well as other embodiments will become apparent from the detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a plot of the conversion of n-heptane achieved by selected catalysts made in Example 1.

[0014] FIG. 2 is a plot of the selectivities of the catalysts of FIG. 1 for n-heptane isomerization.

[0015] FIG. 3 is a plot of the selectivities of the catalysts of FIG. 1 for the isomerization of n-heptane to 2,2-dimethylpentane and 2,4-dimethylpentane.

[0016] FIG. 4 is a plot of the yields of the catalysts of FIG. 1 for the isomerization of n-heptane to 2,2-dimethylpentane and 2,4-dimethylpentane.

[0017] FIG. 5 is a plot of the conversion of n-heptane achieved by selected catalysts made in Example 1 where ytterbium is a modifier.

[0018] FIG. 6 is a plot of the selectivities of the catalysts of FIG. 5 for n-heptane isomerization.

[0019] FIG. 7 is a plot of the selectivities of the catalysts of FIG. 5 for the isomerization of n-heptane to 2,2-dimethylpentane and 2,4-dimethylpentane.

[0020] FIG. 8 is a plot of the yields of the catalysts of FIG. 5 for the isomerization of n-heptane to 2,2-dimethylpentane and 2,4-dimethylpentane.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The support material of the catalyst of the present invention comprises an oxide or hydroxide of a Group IVB (IUPAC 4) metal, see Cotton and Wilkinson, Advanced Inorganic Chemistry, John Wiley & Sons (Fifth Edition, 1988) and including zirconium, titanium and hafnium. Preferably, the metal is selected from zirconium and titanium, with zirconium being especially preferred. The preferred zirconium oxide or hydroxide is converted via calcination to crystalline form. Tungstate is composited on the support material to form, it is believed without so limiting the invention, a mixture of Brönsted and Lewis acid sites. A component of at least one lanthanide-series element, yttrium, or mixtures thereof, is incorporated into the composite by any suitable means. A platinum-group metal component is added to the catalytic composite by any means known in the art to effect the catalyst of the invention, e.g., by impregnation. Optionally, the catalyst is bound with a refractory inorganic oxide. The support, tungstate, metal components, and optional binder may be composited in any order effective to prepare a catalyst useful for the conversion of hydrocarbons, and particularly the isomerization of hydrocarbons.

[0022] Production of the support of the present catalyst may be based on a hydroxide of a Group IVB (IUPAC 4) metal as raw material. For example, suitable zirconium hydroxide is available from MEI of Flemington, New Jersey. Alternatively, the hydroxide may be prepared by hydrolyzing metal oxy-anion compounds, for example $ZrOCl_2$, $ZrO(NO_3)_2$, $ZrO(OH)NO_3$, $ZrOSO_4$, $TiOCl_2$ and the like. Note that commercial $ZrO(OH)_2$ contains a significant amount of

Hf, 1 weight percent. Zirconium alkoxides such as zirconyl acetate and zirconium propoxide may be used as well. The hydrolysis can be effected using a hydrolyzing agent such as ammonium hydroxide, sodium hydroxide, potassium hydroxide, sodium sulfate, $(NH_4)_2HPO_4$ and other such compounds known in the art. The metal oxy-anion component may in turn be prepared from available materials, for example, by treating $ZrOCO_3$ with nitric acid. The hydroxide as purchased or generated by hydrolysis preferably is dried at a temperature of from 100°C to 300°C to vaporize volatile compounds.

[0023] A tungstated support is prepared by treatment with a suitable tungstating agent to form a solid strong acid. Liquid acids whose strength is greater than sulfuric acid have been termed "superacids". A number of liquid superacids are known in the literature including substituted protic acids, e.g., trifluoromethyl substituted H_2SO_4, triflic acid and protic acids activated by Lewis acids (HF plus BF_3). While determination of the acid strength of liquid superacids is relatively straightforward, the exact acid strength of a solid strong acid is difficult to directly measure with any precision because of the less defined nature of the surface state of solids relative to the fully solvated molecules found in liquids. Accordingly, there is no generally applicable correlation between liquid superacids and solid strong acids such that if a liquid super acid is found to catalyze a reaction, there is no corresponding solid strong acid which one can automatically choose to carry out the same reaction. Therefore, as will be used in this specification, "solid strong acids" are those that have an acid strength greater than sulfonic acid resins such as Amberlyst® -15. Additionally, since there is disagreement in the literature whether some of these solid acids are "superacids" only the term solid strong acid as defined above will be used herein. Another way to define a solid strong acid is a solid comprising of interacting protic and Lewis acid sites. Thus, solid strong acids can be a combination of a Bronsted (protonic) acid and a Lewis acid component. In other cases, the Bronsted and Lewis acid components are not readily identified or present as distinct species, yet they meet the above criteria.

[0024] Tungstate ions are incorporated into a catalytic composite, for example, by treatment with ammonium metatungstate in a concentration usually of 0.1 to 20 mass percent tungsten and preferably from 1 to 15 mass percent tungsten. Compounds such as metatungstic acid, sodium tungstate, ammonium tungstate, ammonium paratungstate, which are capable of forming tungstate ions upon calcining, may be employed as alternative sources. Preferably, ammonium metatungstate is employed to provide tungstate ions and form a solid strong acid catalyst. The

tungstate content of the finished catalyst generally is in the range of 0.5 to 25 mass-%, and preferably is from 1 to 25 mass-% on an elemental basis. The tungstate composite is dried, preferably followed by calcination at a temperature of 450°C to 1000°C particularly if the tungstanation is to be followed by incorporation of the platinum-group metal.

[0025] A first component, comprising one or more of the lanthanide-series elements, yttrium, and mixtures thereof, is another essential component of the present catalyst. Included in the lanthanide series are lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Preferred lanthanide series elements include ytterbium, cerium, holmium, europium, and mixtures thereof. Ytterbium and holmium are the most preferred first components of the present catalyst, and it is especially preferred that the first component consists essentially of a ytterbium or holmium component. The first component may in general be present in the catalytic composite in any catalytically available form such as the elemental metal, a compound such as the oxide, hydroxide, halide, oxyhalide, carbonate or nitrate or in chemical combination with one or more of the other ingredients of the catalyst. The first component is preferably an oxide, an intermetallic with platinum, a sulfate, or in the zirconia lattice. The materials are generally calcined between 600°C and 900°C and thus in the oxide form. Although it is not intended to so restrict the present invention, it is believed that best results are obtained when the first component is present in the composite in a form wherein substantially all of the first component is in an oxidation state above that of the elemental state such as in the form of the oxide, oxyhalide or halide or in a mixture thereof and the subsequently described oxidation and reduction steps that are preferably used in the preparation of the instant catalytic composite are specifically designed to achieve this end. The first component can be incorporated into the catalyst in any amount which is catalytically effective, suitably from 0.01 to 10 mass-% first component in the finished catalyst on an elemental basis. Best results usually are achieved with 1 to 5 mass-% of the first component, calculated on an elemental basis.

[0026] The first component is incorporated in the catalytic composite in any suitable manner known to the art, such as by coprecipitation, coextrusion with the porous carrier material, or impregnation of the porous carrier material either before, after, or simultaneously with tungstate though not necessarily with equivalent results. For ease of operation, it is preferred to simultaneously incorporate the first component with the tungstate. It is most preferred to incorporate the platinum-group metal component last. As to the lanthanide element(s), yttrium, or

mixture thereof and the platinum-group metal, the order of addition between the two does not have a significant impact.

[0027] One method of depositing the first component involves impregnating the support with a solution (preferably aqueous) of a decomposable compound of the first component. By decomposable is meant that upon heating, the compound is converted to element or oxide with the release of byproducts. Illustrative of the decomposable compounds without limitation are complexes or compounds such as, nitrates, halides, sulfates, acetates, organic alkyls, hydroxides, and the like compounds. Conditions for decomposition include temperatures ranging from 200°C to 400°C. The first component can be impregnated onto the carrier either prior to, simultaneously with, or after the platinum-group metal component, although not necessarily with equivalent results. If a sequential technique is used, the composite can be dried or dried and calcined in between impregnations.

[0028] A second component, a platinum-group metal, is an essential ingredient of the catalyst. The second component comprises at least one of platinum, palladium, ruthenium, rhodium, iridium, or osmium; platinum is preferred, and it is especially preferred that the platinum-group metal consists essentially of platinum. The platinum-group metal component may exist within the final catalytic composite as a compound such as an oxide, sulfide, halide, oxyhalide, etc., in chemical combination with one or more of the other ingredients of the composite or as the metal. Amounts in the range of from 0.01 to 2 mass-% platinum-group metal component, on an elemental basis, are effective, and from 0.1 to 1 mass-% platinum-group metal component, on an elemental basis, are preferred . Best results are obtained when substantially all of the platinum-group metal is present in the elemental state.

[0029] The second component, a platinum-group metal component, is deposited on the composite using the same means as for the first component described above. Illustrative of the decomposable compounds of the platinum group metals are chloroplatinic acid, ammonium chloroplatinate, bromoplatinic acid, dinitrodiamino platinum, sodium tetranitroplatinate, rhodium trichoride, hexa-amminerhodium chloride, rhodium carbonylchloride, sodium hexanitrorhodate, chloropalladic acid, palladium chloride, palladium nitrate, diamminepalladium hydroxide, tetraamminepalladium chloride, hexachloroiridate (IV) acid, hexachloroiridate (III) acid, ammonium hexachloroiridate (III), ammonium aquohexachloroiridate (IV), ruthenium tetrachloride, hexachlororuthenate, hexa-ammineruthenium chloride, osmium trichloride and ammonium osmium chloride. The second

component, a platinum-group component, is deposited on the support either before, after, or simultaneously with tungstate and/or the first component though not necessarily with equivalent results. It is preferred that the platinum-group component is deposited on the support either after or simultaneously with tungstate and/or the first component.

[0030] In addition to the first and second components above, the catalyst may optionally further include a third component of iron, cobalt, nickel, rhenium or mixtures thereof. Iron is preferred, and the iron may be present in amounts ranging from 0.1 to 5 mass-% on an elemental basis. The third component, such as iron, may function to lower the amount of the first component, such as ytterbium, needed in the optimal formulation. The third component may be deposited on the composite using the same means as for the first and second components as described above. When the third component is iron, suitable compounds would include iron nitrate, iron halides, iron sulfate and any other soluble iron compound.

[0031] The catalytic composite described above can be used as a powder or can be formed into any desired shapes such as pills, cakes, extrudates, powders, granules, spheres, etc., and they may be utilized in any particular size. The composite is formed into the particular shape by means well known in the art. In making the various shapes, it may be desirable to mix the composite with a binder. However, it must be emphasized that the catalyst may be made and successfully used without a binder. The binder, when employed, usually comprises from 0.1 to 50 mass-%, preferably from 5 to 20 mass-%, of the finished catalyst. Refractory inorganic oxide are suitable binders. Examples of binders without limitation are silica, aluminas, silica-alumina, magnesia, zirconium and mixtures thereof. A preferred binder material is alumina, with eta- and/or especially gamma-alumina being favored. Usually the composite and optional binder are mixed along with a peptizing agent such as HCl, HNO_3, KOH, etc. to form a homogeneous mixture which is formed into a desired shape by forming means well known in the art. These forming means include extrusion, spray drying, oil dropping, marumarizing, conical screw mixing, etc. Extrusion means include screw extruders and extrusion presses. The forming means will determine how much water, if any, is added to the mixture. Thus, if extrusion is used, then the mixture should be in the form of a dough, whereas if spray drying or oil dropping is used, then enough water needs to be present in order to form a slurry. These particles are calcined at a temperature of 260°C to 650°C for a period of 0.5 to 2 hours.

[0032] The catalytic composites of the present invention either as synthesized or after calcination can be used as catalysts in hydrocarbon conversion processes. Calcination is

required, for example, to form zirconium oxide from zirconium hydroxide. Hydrocarbon conversion processes are well known in the art and include cracking, hydrocracking, alkylation of both aromatics and isoparaffins, isomerization, polymerization, reforming, dewaxing, hydrogenation, dehydrogenation, transalkylation, dealkylation, hydration, dehydration, hydrotreating, hydrodenitrogenation, hydrodesulfurization, methanation, ring opening, and syngas shift processes. Specific reaction conditions and the types of feeds, which can be used in these processes, are set forth in US 4,310,440 and US 4,440,871, which are hereby incorporated by reference. A preferred hydrocarbon conversion process is the isomerization of paraffins.

[0033] In a paraffin isomerization process, common naphtha feedstocks boiling within the gasoline range contain paraffins, naphthenes, and aromatics, and may comprise small amounts of olefins. Feedstocks which may be utilized include straight-run naphthas, natural gasoline, synthetic naphthas, thermal gasoline, catalytically cracked gasoline, partially reformed naphthas or raffinates from extraction of aromatics. The feedstock essentially is encompassed by the range of a full-range naphtha, or within the boiling point range of 0°C to 230°C.

[0034] The principal components of the preferred feedstock are alkanes and cycloalkanes having from 4 to 10 carbon atoms per molecule, especially those having from 7 to 8 carbon atoms per molecule. Smaller amounts of aromatic and olefinic hydrocarbons also may be present. Usually, the concentration of C_7 and heavier components is more than 10 mass-% of the feedstock. Although there are no specific limits to the total content in the feedstock of cyclic hydrocarbons, the feedstock generally contains between 2 and 40 mass-% of cyclics comprising naphthenes and aromatics. The aromatics contained in the naphtha feedstock, although generally amounting to less than the alkanes and cycloalkanes, may comprise from 0 to 20 mass-% and more usually from 0 to 10 mass-% of the total. Benzene usually comprises the principal aromatics constituent of the preferred feedstock, optionally along with smaller amounts of toluene and higher-boiling aromatics within the boiling ranges described above.

[0035] Contacting within the isomerization zones may be effected using the catalyst in a fixed-bed system, a moving-bed system, a fluidized-bed system, or in a batch-type operation. A fixed-bed system is preferred. The reactants may be contacted with the bed of catalyst particles in either upward, downward, or radial-flow fashion. The reactants may be in the liquid phase, a mixed liquid-vapor phase, or a vapor phase when contacted with the catalyst particles, with excellent results being obtained by application of the present invention to a primarily liquid-phase

operation. The isomerization zone may be in a single reactor or in two or more separate reactors with suitable means therebetween to ensure that the desired isomerization temperature is maintained at the entrance to each zone. Two or more reactors in sequence are preferred to enable improved isomerization through control of individual reactor temperatures and for partial catalyst replacement without a process shutdown.

[0036] Isomerization conditions in the isomerization zone include reactor temperatures usually ranging from 25°C to 300°C. Lower reaction temperatures are generally preferred in order to favor equilibrium mixtures having the highest concentration of high-octane highly branched isoalkanes and to minimize cracking of the feed to lighter hydrocarbons. Temperatures in the range of 100°C to 250°C are preferred in the process of the present invention. Reactor operating pressures generally range from 100 kPa to 10 MPa absolute, preferably between 0.3 and 4 MPa. Liquid hourly space velocities range from 0.2 to 25 hr^{-1}, with a range of 0.5 to 10 hr^{-1} being preferred.

[0037] Hydrogen is admixed with or remains with the paraffinic feedstock to the isomerization zone to provide a mole ratio of hydrogen to hydrocarbon feed of from 0.01 to 20, preferably from 0.05 to 5. The hydrogen may be supplied totally from outside the process or supplemented by hydrogen recycled to the feed after separation from the reactor effluent. Light hydrocarbons and small amounts of inerts such as nitrogen and argon may be present in the hydrogen. Water should be removed from hydrogen supplied from outside the process, preferably by an adsorption system as is known in the art. In a preferred embodiment, the hydrogen to hydrocarbon mol ratio in the reactor effluent is equal to or less than 0.05, generally obviating the need to recycle hydrogen from the reactor effluent to the feed.

[0038] Upon contact with the catalyst, at least a portion of the paraffinic feedstock is converted to desired, higher octane, isoparaffin products. The catalyst of the present invention provides the advantages of high activity and improved stability.

[0039] The isomerization zone generally also contains a separation section, optimally comprising one or more fractional distillation columns having associated appurtenances and separating lighter components from an isoparaffin-rich product. Optionally, a fractionator may separate an isoparaffin concentrate from a cyclics concentrate with the latter being recycled to a ring-cleavage zone.

[0040] Preferably part or all of the isoparaffin-rich product and/or the isoparaffin concentrate are blended into finished gasoline along with other gasoline components from refinery processing

including, but not limited to, one or more of butanes, butenes, pentanes, naphtha, catalytic reformate, isomerate, alkylate, polymer, aromatic extract, heavy aromatics, gasoline from catalytic cracking, hydrocracking, thermal cracking, thermal reforming, steam pyrolysis and coking, oxygenates such as methanol, ethanol, propanol, isopropanol, tert-butyl alcohol, sec-butyl alcohol, methyl tertiary butyl ether, ethyl tertiary butyl ether, methyl tertiary amyl ether and higher alcohols and ethers, and small amounts of additives to promote gasoline stability and uniformity, avoid corrosion and weather problems, maintain a clean engine and improve driveability.

[0041] The following examples serve to illustrate certain specific embodiments of the present invention. These examples should not, however, be construed as limiting the scope of the invention as set forth in the claims. There are many possible other variations, as those of ordinary skill in the art will recognize, which are within the scope of the invention.

EXAMPLE 1

[0042] Catalyst samples of Table 1 were prepared starting with zirconium hydroxide that had been prepared by precipitating zirconyl nitrate with ammonium hydroxide at 65°C. The zirconium hydroxide was dried at 120°C, ground to 40-60 mesh. Multiple discrete portions of the zirconium hydroxide were prepared. Solutions of either ammonium metatungstate or a metal salt (component 1) were prepared and added to the portions of zirconium hydroxide. The materials were agitated briefly and then dried with 80°C to 100°C air while rotating. The impregnated samples were then dried in a muffle oven at 150°C for 2 hours under air. Solutions of a metal salt (component 2, where component 2 is not the same as component 1) were prepared and added to the dried materials. The samples were briefly agitated and dried while rotating. The samples were then calcined at 600°C to 850°C for 5 hours. The final impregnation solutions of chloroplatinic acid were prepared and added to the solids. The samples were agitated and dried while rotating as before. The samples were finally calcined at 525°C in air for 2 hours. In Table 1 below, it can be seen that the catalysts were made at modifier levels of 2.5 mass-% and 5 mass-%; tungstate levels of 5 mass-%, 10 mass-%, and 15 mass-%; and calcination temperatures of 650°C, 700°C, 750°C, 800°C, and 850°C (with the exception of Gd, which was only prepared at 650°C, 700°C, and 750°C calcination temperatures).

[0043] For example, the first row of Table 1 indicates that a total of 30 different catalysts were made, a catalyst having 2.5 mass-% Ce and 5 mass-% WO_4 and calcined at 650°C, a

catalyst having 5 mass-% Ce and 5 mass-% WO_4 and calcined at 650°C, a catalyst having 2.5 mass-% Ce and 10 mass-% WO_4 and calcined at 650°C, a catalyst having 5 mass-% Ce and 10 mass-% WO_4 and calcined at 650°C, a catalyst having 2.5 mass-% Ce and 15 mass-% WO_4 and calcined at 650°C, a catalyst having 5 mass-% Ce and 15 mass-% WO_4 and calcined at 650°C; a catalyst having 2.5 mass-% Ce and 5 mass-% WO_4 and calcined at 700°C, a catalyst having 5 mass-% Ce and 5 mass-% WO_4 and calcined at 700°C, a catalyst having 2.5 mass-% Ce and 10 mass-% WO_4 and calcined at 700°C, a catalyst having 5 mass-% Ce and 10 mass-% WO_4 and calcined at 700°C, a catalyst having 2.5 mass-% Ce and 15 mass-% WO_4 and calcined at 700°C, a catalyst having 5 mass-% Ce and 15 mass-% WO_4 and calcined at 700°C; a catalyst having 2.5 mass-% Ce and 5 mass-% WO_4 and calcined at 750°C, a catalyst having 5 mass-% Ce and 5 mass-% WO_4 and calcined at 750°C, a catalyst having 2.5 mass-% Ce and 10 mass-% WO_4 and calcined at 750°C, a catalyst having 5 mass-% Ce and 10 mass-% WO_4 and calcined at 750°C, a catalyst having 2.5 mass-% Ce and 15 mass-% WO_4 and calcined at 750°C, a catalyst having 5 mass-% Ce and 15 mass-% WO_4 and calcined at 750°C, a catalyst having 2.5 mass-% Ce and 5 mass-% WO_4 and calcined at 800°C, a catalyst having 5 mass-% Ce and 5 mass-% WO_4 and calcined at 800°C, a catalyst having 2.5 mass-% Ce and 10 mass-% WO_4 and calcined at 800°C, a catalyst having 5 mass-% Ce and 10 mass-% WO_4 and calcined at 800°C, a catalyst having 2.5 mass-% Ce and 15 mass-% WO_4 and calcined at 800°C, a catalyst having 5 mass-% Ce and 15 mass-% WO_4 and calcined at 800°C, a catalyst having 2.5 mass-% Ce and 5 mass-% WO_4 and calcined at 850°C, a catalyst having 5 mass-% Ce and 5 mass-% WO_4 and calcined at 850°C, a catalyst having 2.5 mass-% Ce and 10 mass-% WO_4 and calcined at 850°C, a catalyst having 5 mass-% Ce and 10 mass-% WO_4 and calcined at 850°C, a catalyst having 2.5 mass-% Ce and 15 mass-% WO_4 and calcined at 850°C, a catalyst having 5 mass-% Ce and 15 mass-% WO_4 and calcined at 850°C; with all catalysts listed above also having 0.5 mass-% platinum. Therefore, Table 1 represents a total of 228 different catalysts that were made.

TABLE 1

Modifier	Modifier Level mass-%		Pt mass-%	WO_4 Levels Mass-%			Calcination Temp, °C				
Ce	2.5	5	0.5	5	10	15	650	700	750	800	850
Eu	2.5	5	0.5	5	10	15	650	700	750	800	850
Gd	2.5	5	0.5	5	10	15	650	700	750	------	------
Ho	2.5	5	0.5	5	10	15	650	700	750	800	850
Nd	2.5	5	0.5	5	10	15	650	700	750	800	850
Re	2.5	5	0.5	5	10	15	650	700	750	800	850
Y	2.5	5	0.5	5	10	15	650	700	750	800	850
Yb	2.5	5	0.5	5	10	15	650	700	750	800	850

EXAMPLE 2

[0044] The catalysts of Example 1 were prepared as described above in Example 1. Also, reference catalysts were prepared as described in Example 1 but with the addition of the modifier step being omitted from the preparation. Approximately 95 mg of each sample was loaded into a multi-unit reactor assay. The catalysts were pretreated in air at 450°C for 6 hours and reduced at 200°C in H_2 for 1 hour. n-Heptane, 8 mol-%, in hydrogen was then passed over the samples at 120°C, 150°C, and 180°C, approximately 1 atm, and 0.3, 0.6, and 1.2 hr^{-1} WHSV (based on heptane only). The products were analyzed using online gas chromatographs.

[0045] To exemplify the data, selected results are shown in FIGs. 1 – 4 for experiments at 180°C, 1.2 hr^{-1} WHSV, and using catalysts comprising 15 mass-% W, 0.5 mass-% Pt. The identity of the modifier (or first component), the amount of modifier, and the calcination temperature are identified along the x-axis of the plots of FIGs. 1 - 4. Data where the identity of the modifier is listed as "none", corresponds to a reference catalyst containing no modifier. FIG. 1 is a plot of the conversion of heptane achieved by each of the catalysts. All of the catalysts indicate activity, with ytterbium, yttrium, and holmium showing the greatest conversion. It is surprising, however, that many of the catalysts demonstrate the greatest conversion when calcined at 800°C. The more expected trend would be a decreasing conversion trend with increasing calcination temperatures. A number of the catalysts of the

present invention however, exhibit greater conversion with a calcination at 800°C than at either 750°C or 850°C. Therefore, a preferred calcination temperature is at 800°C.

[0046] FIG. 2 shows the selectivity of the catalysts for C_7 isomerization. This plot demonstrates that even though some cracking is occurring, selectivities to C_7 isomerization remain high. FIG. 3 shows the selectivity of the catalysts for C_7 isomerization to produce two of the desired dimethyl-branched isomers, 2,2-dimethylpentane and 2,4-dimethylpentane. Again, the data demonstrates that ytterbium and yttrium show superior results and are therefore, preferred modifiers. Fig. 4 shows the yield of the catalysts for C_7 isomerization to produce two desired dimethyl-branched isomers, 2,2-dimethylpentane and 2,4-dimethylpentane.

[0047] The data discussed above indicates a particular preference for ytterbium as a modifier. Therefore, FIGs. 5-8 present further selected results of the experiment where ytterbium was the modifier. On each of FIGs. 5-8, the amount of tungsten on the catalyst, the amount of modifier on the catalyst, the calcination temperature of the catalyst, and the weight hourly space velocity of the run is found on the x-axis. In FIG. 5, the y-axis is the conversion of the n-heptane feed. The plot demonstrates that conversion increases as the amount of tungsten increases, but conversion decreases as the weight hourly space velocity increases. However, with other variables remaining constant, increasing the amount of modifier from 2.5 mass-% to 5 mass-% does not have a dramatic effect on the conversion. FIG. 6 demonstrates that the selectivity for C_7 isomerization increases with increasing space velocity. However, FIG. 7 shows that the opposite is true when considering the selectivity to two of the desired dimethyl-branched isomers, 2,2-dimethylpentane and 2,4-dimethylpentane. FIG. 8 shows the yield of two of the desired dimethyl-branched isomers, 2,2-dimethylpentane and 2,4-dimethylpentane. In general, the results in FIG. 8 indicate that the yield to the specific dimethylpentane isomers (1) decreases as the space velocity is increased; (2) is highest with a calcination temperature of 800°C; and (3) is greater at the lower levels of modifiers.

CLAIMS:

1. A catalyst comprising a support comprising a tungstated oxide or hydroxide of at least one of the elements of Group IVB (IUPAC 4) of the Periodic Table, the support having deposited thereon; a first component selected from the group consisting of at least one lanthanide series element, yttrium, and mixtures thereof; and a second component comprising at least one platinum-group metal component or a mixture thereof.
2. The catalyst of Claim 1, wherein the first component comprises from 0.01 to 10 mass-%, on an elemental basis, of the catalyst, the second component comprises from 0.01 to 2 mass-%, on an elemental basis, of the catalyst and the catalyst comprises from 0.5 to 25 mass-% tungsten on an elemental basis.
3. The catalyst of Claim 1 or 2 wherein the element of Group IVB (IUPAC 4) comprises zirconium and the first component is selected from the group consisting of ytterbium, yttrium, cerium, holmium, europium, and combinations thereof.
4. The catalyst of Claim 1, 2, or 3 further comprising from 0.1 to 50 mass-% of a refractory inorganic-oxide binder.
5. The catalyst of any one of the preceding claims further comprising a third component selected from the group consisting of iron, cobalt, nickel, rhenium, and mixtures thereof wherein the third component is present in an amount from 0.1 to 5 mass-%.
6. The catalyst of any one of the preceding claims, wherein the first component is selected from the group consisting of ytterbium, yttrium, cerium, holmium, europium, or mixtures thereof and the second component is platinum.
7. A process for converting hydrocarbons by contacting a feed with a solid acid catalyst according to any one of the preceding claims to generate a converted product, wherein the hydrocarbon conversion process is selected from the group consisting of cracking, hydrocracking, aromatic alkylation, isoparaffin alkylation, isomerization, polymerization, reforming, dewaxing, hydrogenation, dehydrogenation, transalkylation, dealkylation, hydration, dehydration, hydrotreating, hydrodenitrogenation, hydrodesulfurization, methanation, ring opening, and syngas shift.
8. A process for the isomerization of a paraffinic feedstock to obtain a product having an increased isoparaffin content comprising contacting the paraffinic feedstock in an isomerization zone maintained at isomerization conditions comprising a temperature from

25°C to 300°C, a pressure from 100 kPa to 10 MPa and liquid hourly space velocity from 0.2 to 15 hr^{-1} with a solid acid isomerization catalyst according to any one of claims 1 to 7, and recovering an isoparaffin-rich product.

9. The process of Claim 7 or 8 wherein the isomerization conditions comprise a temperature from 100°C to 250°C, a pressure from 300 kPa to 4 MPa, and a liquid hourly space velocity from 0.5 to 15 hr^{-1}, and wherein free hydrogen is present in the isomerization zone in an amount from 0.01 to 20 moles per mole of C_5+ hydrocarbons present in the zone.
10. The process of Claim 7, 8 or 9, further comprising using at least a portion of the isoparaffin-rich product to blend a gasoline product.