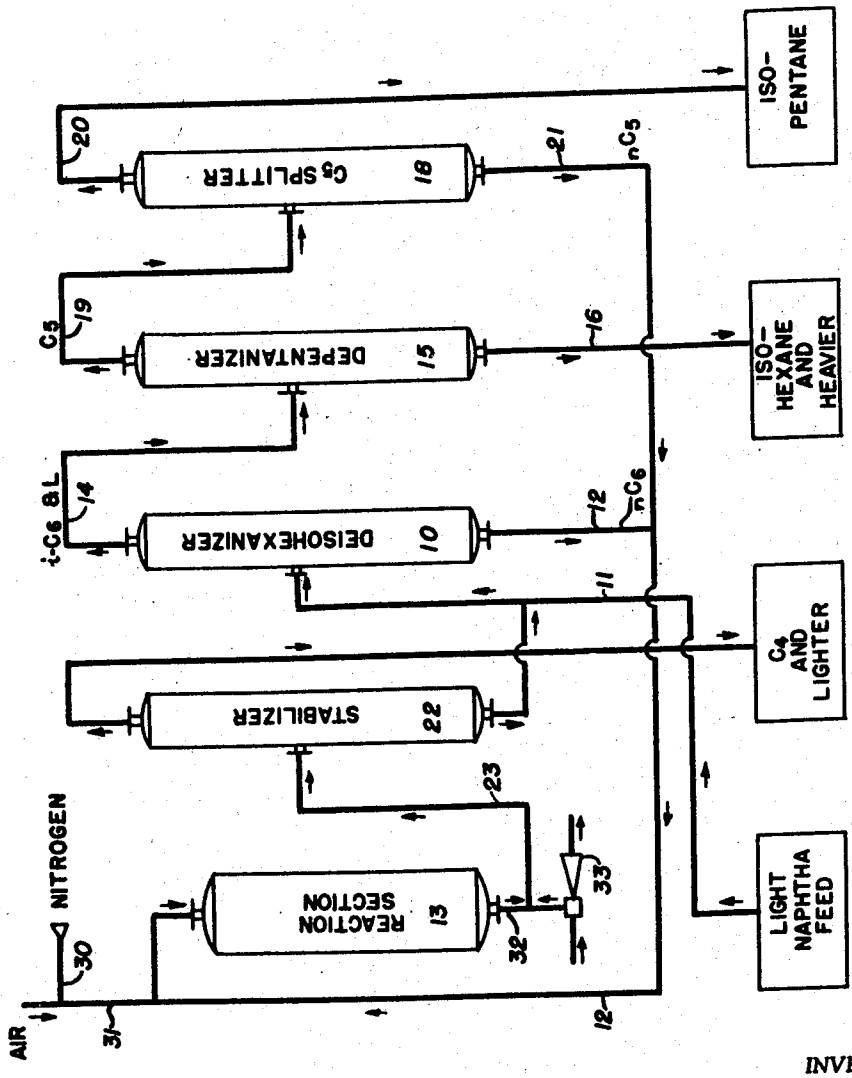
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PROCESS AND CATALYST FOR THE ISOMERIZATION OF HYDROCARBONS

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INVENTORS
HILLIS O. FOLKINS
ELMER L. MILLER
KENNETH E. LUCAS

BY Edward H. Lang

ATTORNEY

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PROCESS AND CATALYST FOR THE ISOMERIZATION OF HYDROCARBONS

Hillis O. Folkins, Crystal Lake, Elmer L. Miller, Cary, and Kenneth E. Lucas, Crystal Lake, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

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This invention relates to the catalytic hydroisomerization of isomerizable hydrocarbons having 4 to 7 carbon atoms per molecule. It is more specifically concerned with improving the octane rating of petroleum hydrocarbon feed stocks consisting predominately of normal hexane and/or normal pentane hydrocarbons.

According to this invention it has been found that the hydroisomerization of hydrocarbon feed stocks consisting predominately of isomerizable saturated hydrocarbons having 4 to 7 carbon atoms per molecule can be efficiently carried out by processing the feed stocks at a temperature within the range of about 650 to 800° F., a pressure within the range of 100 to 1000 p.s.i.g., and a hydrogen-hydrocarbon mol ratio within the range of about 0.5 to 5, in the presence of a composite catalyst consisting essentially of a major portion of a silica-alumina hydrocarbon cracking catalyst containing not less than about 50% by weight of silica and having incorporated therein minor concentrations of a combination of metallic palladium and rhodium wherein palladium is present in a quantity exceeding the rhodium portion.

In an integrated petroleum refining process for the production of high-octane-number gasolines, in order to obtain maximum effectiveness one of the unit processes must be selected for the processing of feed stocks consisting predominately of the lower-molecular-weight, normally liquid, saturated hydrocarbons containing 4 to 7 carbon atoms per molecule. Substantial quantities of these feed stocks are available to warrant the separate processing of these materials. Although octane number improvement can be obtained by treating these feed stocks in a dehydrogenation process to produce olefins, it is more desirable from an octane-yield relationship to utilize isomerization processes for effecting the octane number improvement in these compositions. Furthermore, the isomerization product has an increased research octane number and improved road performance and is a stable product which augments the stability of the blended finished gasoline.

Because of the importance of isomerization as a unit process for use in an integrated refining scheme for the production of high-octane-number gasolines, a number of commercial isomerization processes have been developed which utilize a solid catalyst. The use of such catalysts eliminates the plant corrosion problems and accompanying high maintenance costs which were attendant upon the use of the so-called Friedel-Crafts catalysts. Because of the effectiveness of platinum-promoted catalyst composites, such as platinum-halogen-alumina, platinum-silica-alumina, etc. in hydroforming operations, it has been natural to utilize these same catalysts in isomerization processes. These catalysts, however, require higher operating temperatures which are disadvantageous because isomerization is an equilibrium reaction whose efficiency decreases with an increase in the processing temperature. As a result, at the higher temperatures employed, the equilibrium product contains substantial quantities of low-octane-number paraffins which are not isomerized during

the course of the reaction. In addition, it has been reported that as the equilibrium conversion is approached, the gas loss increases very sharply. Further disadvantages resulting from the use of high-temperature processing conditions are higher fuel costs for carrying out the reaction, as well as added expense for fabricating process vessels to withstand the combination of high pressures and high temperatures required for this type of isomerization. A non-platinum-containing noble metal catalyst, however, has been found which permits the isomerization reaction to be carried out at lower operating temperatures which avoid the disadvantages accompanying high-temperature isomerization using platinum-type solid catalysts.

It is therefore the primary objective of this invention to provide a hydroisomerization process for the isomerization of hydrocarbon feed stocks consisting predominately of low-molecular-weight isomerization hydrocarbons having 4 to 7 carbon atoms per molecule. It is another object of this invention to provide a process for the octane number improvement of petroleum-derived feed stocks consisting essentially of C_5–C_6 normal paraffinic hydrocarbons. It is an additional object of this invention to carry out the hydroisomerization process employing a solid, non-corrosive catalyst utilizing a relatively low-temperature operation which permits one to obtain a substantial production of branch-chain isomerization products with a minimum loss to gaseous products consisting of butanes and lower-molecular-weight hydrocarbons.

These and other objects will become more apparent from the following detailed description of this invention.

The figure is illustrative of a processing scheme employing the process of this invention.

According to this invention, it has been found that catalysts consisting essentially of a major portion of a silica-alumina hydrocarbon cracking catalyst containing not less than about 50% by weight of silica, and having incorporated therein a minor quantity of a combination of metallic palladium and rhodium wherein palladium is present in a quantity exceeding the rhodium portion, exhibit high activity and selectivity for the isomerization of saturated isomerizable hydrocarbons having 4 to 7 carbons atoms per molecule. These catalysts operate efficiently at reaction temperatures not in excess of about 800° F. In carrying out the process of this invention, a composite catalyst containing a combination of 0.05–0.7% of metallic palladium, and 0.01–0.2% by weight of metallic rhodium, based on total catalyst composition, wherein the palladium is present in a quantity exceeding the rhodium portion, said combination being incorporated in a major portion of a silica-alumina hydrocarbon cracking catalyst containing more than 50% by weight of silica, based on said cracking catalyst, is employed to accelerate the hydroisomerization of saturated, isomerizable hydrocarbons having 4 to 7 carbon atoms per molecule under the following operating conditions.

	Range	Preferred Range
Temperature, ° F., for:		
n-C_4	700–800	725–800
n-C_5	680–775	700–760
n-C_6	650–740	675–725
n-C_7	600–725	625–700
Pressure, p.s.i.g.	100–1,000	350–750
Liquid Hourly Volume Space Velocity [1]	0.5–10	1–4
H_2/hydrocarbon mol ratio	0.5–5	1.5–4.5

[1] The liquid volume, not applicable to C_4, of limiting reactant fed per hour per unit volume of effective catalyst bed.

In the isomerization process of this invention a variety of processing schemes are available. In the drawing is shown a simple scheme which utilizes a feed preparation

and product recovery system employing a minimum number of process towers. A light, straight-run naphtha feed having an ASTM boiling range of about 100°–180° F. is introduced into deisohexanizer 10 via line 11. The bottoms consisting essentially of n-hexane and heavier hydrocarbons is sent through line 12 to reactor 13 for isomerization. The isohexane and lighter hydrocarbons are removed from deisohexanizer 10 and transferred by means of line 14 to depentanizer 15 where the isohexane and heavier hydrocarbons are separated and removed from the system via line 16 to storage. The overhead from depentanizer 15, which consists essentially of normal and isopentane, is sent to C_5-splitter 18 through line 19. Isopentane is recovered in the fractionator overhead, and transferred to storage through line 20, or to suitable gasoline blending facilities (not shown), and the bottoms produced, consisting predominately of normal pentane, is transferred by means of line 21 to a point of confluence with line 12 wherein it is sent to reactor 13 for processing. The reaction effluent is transferred through line 23 to stabilizer 22 where the butane-and-lighter fraction is separated. The pentane-and-heavier fraction is then processed in deisohexanizer 10 as above.

Catalysts employed in carrying out the process of this invention are prepared by conventional catalyst preparation techniques by incorporating a small amount of a combination of metallic palladium and rhodium in a hydrocarbon cracking catalyst consisting of a silica-alumina composite containing more than 50% silica. The combination of metallic palladium and rhodium is incorporated in the silica-alumina support by impregnation of the support with soluble salts or complexes of palladium and rhodium, e.g., an acid solution of the metal chlorides, such as a hydrochloric acid solution of rhodium chloride and palladium chloride; or the mixed salts of the acids produced, e.g., ammonium chlororhodinate and ammonium chloropalladinate; or nitrito, amino, and nitrito-amine complexes of these metals, e.g., ammonium hexachloropalladinate or ammonium hexachlororhodinate. Colloidal solutions of salts of palladium and rhodium can also be used as the impregnant. The metallic constituents of the catalyst composition can be introduced either sequentially, with either constituent being initially introduced, or simultaneously by co-impregnation with the selected impregnants. The preparation of the supported catalyst is generally carried out by wetting the support with an aqueous solution of rhodium chloride and palladium chloride. The quantity of metallic palladium and rhodium incorporated in the silica-alumina support can vary between about 0.06–1% by weight, based on catalyst composition. It has been found that optimum effectiveness is obtained if an amount within the range of 0.2 to 0.6 wt. percent is employed.

Prior to impregnating the silica-alumina support, it is preferred that this component of the catalyst composition be dried at an elevated temperature within the range of about 250–400° F. The impregnated mass is dried for at least about 4 hours at a temperature within the range of 225–350° F. The "green" catalyst is then pelleted and activated by contacting the dried catalyst mass with a reducing stream of hydrogen at an elevated temperature for a time sufficient to reduce the palladium and rhodium components of the "green" catalyst to the metallic state. This reduction can generally be effected by heating the catalyst mass to 975° F. in hydrogen over a period of about five hours followed by continued treatment with hydrogen at 975° F. for sixteen hours. In general 2000 to 5000 s.c.f.h./barrel of catalyst are used, and this phase of the catalyst preparation is carried out for 2 to 16 hours.

After the reduction, substantially all of the palladium and rhodium will be in the metallic form; however, small amounts can remain in an oxidized condition without deleteriously affecting the efficiency of the catalysts.

In selecting the silica-alumina, hydrocarbon-cracking catalysts for use in the preparation of the isomerization catalyst employed in the process of this invention, it is necessary that the composition contain not less than about 50% by weight of silica. Accordingly, the hydrocarbon-cracking catalysts will have a silica content within the range of about 50–95% by weight, and preferably 75–92%, and an alumina content within the range of about 50–5%, preferably 8–25%. The silica-alumina support can be obtained commercially or can be prepared by admixing separately prepared portions of silica gel and alumina gel or in the alternative by conventional co-precipitation techniques. It is also possible to prepare a catalyst which can be employed in the instant invention by contacting silica gel particles with a solution of an aluminum salt and rhodium and palladium salts of the desired concentrations. After drying the mixture, it is heated for a sufficient time to effect the decomposition of the salts. Thereafter the group VIII metals are reduced to the metallic state by treatment with hydrogen at elevated temperatures employing the above-described conditioning technique.

The process of this invention is especially adaptable for effecting the isomerization of feed stocks consisting predominately of normal pentane and/or normal hexane hydrocarbons to produce an octane improvement by promoting the molecular rearrangement of the saturated hydrocarbons, or mixtures thereof, such as light petroleum fractions having a boiling range of 100° F.–200° F.

The invention is further illustrated by the following non-limiting and illustrative example of the use of a palladium-rhodium, silica-alumina composite catalyst in the isomerization of low-boiling, saturated, isomerizable hydrocarbon having 4 to 7 carbon atoms.

A palladium-rhodium, silica-alumina catalyst was prepared by impregnating a silica-alumina support having the following composition:

Composition:	Weight percent
Alumina	24.4
Na_2O	0.021
SO_4	0.25
Fe	0.25
SiO_2	75.3

with an acidified aqueous solution of palladium chloride and rhodium chloride. The solution was prepared by dissolving 2.0 grams of palladium chloride and 0.5 gram of rhodium chloride in about 1 normal hydrochloric acid. To prepare a catalyst containing 0.48% by weight of metallic palladium and 0.1% by weight of metallic rhodium, based on total catalyst composition, on a silica-alumina support consisting nominally of 75% by weight of silica and 25% by weight of alumina, 250 grams of silica-alumina were placed in a suitable vessel containing 250 ml. of palladium chloride-rhodium chloride solution. This volume of solution represented the average amount necessary to fill the actual pore volume of the silica-alumina support employed. If some other silica-alumina is employed, a volume of solution compatible with the adsorptive capacity of that support should be used. The impregnated support was dried at about 230° F. for sixteen hours, and subsequently pelleted into ⅛-inch pellets. Thereafter, 150 cc. of pelleted catalyst was activated by heating to 975° F. in hydrogen over a period of 5 hours, followed by continued treatment with hydrogen at 975° F. for 16 hours. The catalyst was then purged by passing 4 s.c.f.h. of nitrogen through the bed for 1 hour. The catalyst was then oxidized in air at 700° F. Following this, the catalyst was purged with nitrogen and then was heated in a stream of hydrogen to 975° F., after which the reactor was cooled to reaction temperature, pressured to reaction pressure, and the hydrocarbon feed stock charged under desired condition. The advantages of the instant invention are clearly illustrated from the data in Table I. By em-

ploying a combination of metallic palladium and rhodium prepared as above described, wherein the portion of palladium exceeds the quantity of rhodium on the silica-alumina support, a synergistic effect was obtained. The comparative results obtained for silica-alumina, 0.48 palladium-silica-alumina, and 0.1 rhodium-silica-alumina catalysts show that the results obtained in the process of this invention were not evident from an analysis of the conversions, yields and selectivities obtained employing these respective catalysts. That the results obtained employing the process of this invention were unusual is illustrated by the yield data produced by employing silica-alumina compositions containing, respectively, 0.6% by weight of palladium, and 0.6% by weight of rhodium, based on total catalyst composition. The effectiveness of other combinations of palladium and rhodium is also seen.

Table I

Run No.	Catalyst Comp., Percent by wt.				Run Conditions				Feed Composition, Percent by wt.				Conversion Data, Wt. Percent		
	Pd	Rh	SiO_2	Al_2O_3	° F.	P.s.i.g.	LVHSV	H_2/HC	i-C_5	n-C_5	C_6H_{12}	i-C_6	Conversion	Yield	Selectivity
1	0.48	0.1	75	25	700	500	3.02	0.99	1.2	96.8	1.7	0.3	45.7	45.4	99.2
2	0.48		75	25	700	500	3.00	1.00	1.2	96.8	1.7	0.3	38.2	37.0	96.8
3		0.1	75	25	700	500	3.00	1.00	1.2	96.8	1.7	0.3	32.7	32.0	98.0
4	0.6		75	25	700	500	3.00	1.00	1.2	96.8	1.7	0.3	41.1	39.9	97.2
5		0.6	75	25	700	500	3.00	1.00	1.2	96.8	1.7	0.3	34.4	33.9	98.5
6	0.66	0.05	87	13	700	500	3.00	1.04	1.2	96.8	1.7	0.3	49.4	48.3	98.0
7	0.48	0.1	75	25	700	500	3.00	1.01	1.2	96.8	1.7	0.3	45.8	45.4	99.2
8 [1]	0.48	0.1	71	24	700	500	3.00	1.00	1.2	96.8	1.7	0.3	29.4	29.0	98.7
9 [2]	0.48	0.1	65		700	500	3.0	1.0	1.2	96.8	1.7	0.3	4.4	4.2	95.0
10	0.48	0.1	5	95	698	500	3.0	1.0	1.2	96.8	1.7	0.3	13.0	12.2	94.1

[1] Catalyst support also contains 5% ZrO_2.
Pd, Rh percents based on total catalyst weight.
SiO_2 and Al_2O_3 percents based on catalyst support.
[2] Catalyst support also contains 35% MgO.

Another feature of the instant invention is the use of a silica-alumina hydrocarbon-cracking catalyst as the principal constituent of the catalyst employed in the process of this invention. This support was compared with other types of cracking catalysts and the results tabulated in Table I. From these data it is seen that unless a support consisting essentially of a major portion of silica and a minor portion of alumina is employed, the efficiency of the palladium-rhodium metal-containing catalyst is deleteriously affected.

To obtain maximum efficiency, auxiliary equipment is employed for pretreating the feed stock and the hydrogen utilized in the isomerization process. In order to insure long catalyst life, it is necessary to employ a hydrocarbon feed stock which is substantially free from sulfur or sulfur-containing compounds. Accordingly, a pretreater or "guard case" should be installed in the feed line to effect the removal of the sulfur compounds from the feed. Preferably the pretreatment can be effected in a catalytic, vapor-phase, desulfurization process in the presence of clay, bauxite, cobalt molybdate, or other suitable catalysts for effecting the desulfurization of the feed stock in the presence of hydrogen. A variety of desulfurization methods based upon the decomposition of the sulfur compounds at elevated temperatures in the vapor phase are briefly described by Kalichevsky, Petroleum Refiner, vol. 30 (4) at page 117, et seq. It is also preferred that the hydrogen employed as a processing aid in the hydroisomerization process be substantially free of water, O_2, CO, H_2S and related compounds, including those which react under hydroisomerization conditions to form the above. Although it is preferred that the hydrogen be free of these impurities, trace amounts of these substances not in excess of about 2 parts per million can be tolerated.

The palladium-rhodium-promoted, silica-alumina, composite catalyst employed in the hydroisomerization process of this invention can be regenerated in situ, thereby providing a continuous regenerative isomerization process. Referring to the drawing, reactivation of the catalyst is provided for by means of the reactivation system shown schematically. Nitrogen from line 30 is fed into line 31 through which air is admitted. Before initiating regeneration, the reaction system is thoroughly purged of hydrocarbons employing hydrogen. Thereafter the reaction system is depressurized to about atmospheric pressure, and purged with heated nitrogen which is passed through line 31 into reactor 13. The purged gases are removed from the system through vent 32. The purging can also be effected by evacuating the system by means of steam ejector 33 which is connected to the system through line 32. After the reactor system has been purged, controlled amounts of air are introduced into the flowing nitrogen stream by means of air supply-line 31 and the air-nitrogen mixture is passed through the reactor to oxidize the deactivated catalyst. The initial oxidation is carried out at a temperature of about 700° F. employing a "flash burn-out." When this phase of the regeneration is completed, the catalyst temperature is raised to about 975° F. as rapidly as possible employing the air-nitrogen mixture. This mixture is continued in contact with the catalyst for about 1 hour. When the catalyst has been substantially completely oxidized, the reaction system is thoroughly purged with nitrogen, or evacuated using the steam ejector 33, to remove any residual oxygen or other undesirable materials which may have been produced during the oxidation step. Thereafter, the catalyst is reduced with dry hydrogen at a temperature within the range of about 800 to 975° F. This flow of hydrogen is continued for about 2 to 8 hours until the reducible constituents of the catalyst composition are reduced to the metallic state. Thereafter the reactor is cooled to the desired reaction temperature, the reaction system repressured, and fresh feed re-introduced into the reactor.

From the foregoing description of this invention, it is apparent that numerous combinations of reactors and fractionators are possible for carrying out the isomerization process of this invention in the processing of light hydrocarbon feed-stocks. The process of this invention finds application in combination with other conventional unit refining processes, such as reforming, or in split-stream techniques employing a plurality of reactors to separately process feed stocks under isomerization conditions selected to obtain maximum efficiency with respect to the feed stock being processed. The various feed components can be processed jointly or singly, and on a once-through or recycle basis. It will be apparent to those skilled in the art that these modifications can be made without departing from the scope of this invention as defined by the appended claims.

What is claimed is:

1. A hydroisomerization process which comprises processing an isomerizable, saturated hydrocarbon having

4–7 carbon atoms per molecule at a temperature within the range of about 600–800° F., sufficient to effect the isomerization of said hydrocarbon in the substantial absence of hydrocracking, at isomerizing conditions of pressure and H_2/hydrocarbon mol ratio in the presence of an isomerization catalyst consisting essentially of a silica-alumina, hydrocarbon-cracking catalyst composite containing 50–95% by weight of silica and having incorporated therein a small amount of a co-promoter consisting essentially of palladium and rhodium, each being present in an amount sufficient to enhance the isomerization activity of said silica-alumina catalyst, the quantity of palladium present in the catalyst exceeding the amount of rhodium.

2. A hydroisomerization process which comprises processing an isomerizable, saturated hydrocarbon having 4–7 carbon atoms per molecule at a temperature within the range of about 600°–800° F., sufficient to effect the isomerization of said hydrocarbon in the substantial absence of hydrocracking, under isomerizing conditions of pressure and H_2/hydrocarbon mol ratio in the presence of a catalyst consisting essentially of silica-alumina, hydrocarbon-cracking catalyst containing 50–95% by weight of silica and having incorporated therein a co-promoter consisting essentially of 0.05–0.7% by weight of palladium, and 0.01–0.2% by weight of rhodium, based on total catalyst composition, the quantity of palladium present in the catalyst exceeding the amount of rhodium.

3. A hydroisomerization process which comprises processing an isomerizable saturated hydrocarbon having 4–7 carbon atoms per molecule at a temperature within the range of about 600–800° F., sufficient to effect the isomerization of said hydrocarbon in the substantial absence of hydrocracking, under isomerizing conditions of pressure and H_2/hydrocarbon mol ratio in the presence of a catalyst consisting essentially of silica-alumina hydrocarbon-cracking catalyst containing 50–95% by weight of silica and having incorporated therein 0.2–0.6% by weight based on total catalyst composition of a co-promoter consisting essentially of palladium and rhodium, each being present in an amount sufficient to enhance the isomerization activity of said silica-alumina catalyst, the quantity of palladium present in the catalyst exceeding the amount of rhodium.

4. A hydroisomerization process which comprises processing an isomerizable saturated hydrocarbon having 4–7 carbon atoms per molecule at a temperature within the range of about 600–800° F., sufficient to effect the isomerization of said hydrocarbon in the substantial absence of hydrocracking, under isomerizing conditions of pressure and H_2/hydrocarbon mol ratio in the presence of a catalyst consisting essentially of a silica-alumina, hydrocarbon-cracking catalyst containing about 50–95% by weight of silica and 50–5% by weight of alumina, based on said silica-alumina catalyst, having incorporated therein 0.2–0.6% by weight, based on total catalyst composition, of a co-promoter consisting essentially of palladium and rhodium, the quantity of palladium present in the catalyst exceeding the amount of rhodium, and the quantity of rhodium present being not less than about 0.01%.

5. A hydroisomerization process which comprises processing an isomerizable, saturated hydrocarbon having 4–7 carbon atoms per molecule at a temperature within the range of about 600–800° F., sufficient to effect the isomerization of said hydrocarbon in the substantial absence of hydrocracking, a pressure within the range of about 100–1000 p.s.i.g., and a hydrogen/hydrocarbon mol ratio within the range of about 0.5–5 in the presence of a catalyst consisting essentially of silica-alumina, hydrocarbon-cracking catalyst containing 50–95% by weight of silica and having incorporated therein a co-promoter consisting essentially of 0.05–0.7% by weight of palladium, and 0.01–0.2% by weight of rhodium, based on total catalyst composition, the quantity of palladium present in the catalyst exceeding the amount of rhodium.

6. A hydroisomerization process which comprises processing an isomerizable, saturated hydrocarbon having 4–7 carbon atoms per molecule at a temperature within the range of about 600–800° F., sufficient to effect the isomerization of said hydrocarbon in the substantial absence of hydrocracking, a pressure within the range of about 100–1000 p.s.i.g., and a H_2/hydrocarbon mol ratio within the range of about 0.5–5 in the presence of a catalyst consisting essentially of silica-alumina, hydrocarbon-cracking catalyst containing 50–95% by weight of silica and having incorporated therein 0.2–0.6% by weight based on total catalyst composition of a co-promoter consisting essentially of palladium and rhodium, the quantity of palladium present in the catalyst exceeding the amount of rhodium, and the quantity of rhodium present being not less than about 0.01%.

7. A hydroisomerization process which comprises processing a petroleum hydrocarbon feed stock consisting predominantly of straight-chain C_5 and C_6 paraffinic hydrocarbon at a temperature within the range of about 600–775° F., a pressure within a range of about 100–1000 p.s.i.g., and a H_2/hydrocarbon mol ratio within the range of about 0.5–5, in the presence of a catalyst consisting essentially of a silica-alumina, hydrocarbon-cracking catalyst containing about 50–95% by weight of silica and 50–5% by weight of alumina, based on said silica-alumina catalyst, and having incorporated therein 0.2–0.6% by weight, based on total catalyst composition of a co-promoter consisting essentially of palladium and rhodium, the quantity of palladium present in the catalyst exceeding the amount of rhodium, and the quantity of rhodium present being not less than about 0.01%.

8. A process in accordance with claim 7 in which said feed stock consists predominantly of normal pentane and said temperature is within the range of about 680°–775° F.

9. A process in accordance with claim 7 in which said feed stock consists predominantly of normal hexane and said temperature is in the range of about 650°–740° F.

10. A process in accordance with claim 7 in which said silica-alumina hydrocarbon cracking catalyst is calcined at a temperature within the range of about 800° to 1300° F. for a time sufficient to remove the gel water and set the gel structure prior to incorporating the metallic palladium producing agent.

11. A catalyst consisting essentially of a silica-alumina, hydrocarbon-cracking catalyst composite containing 50–95% by weight of silica and having incorporated therein a small amount of a co-promoter consisting essentially of palladium and rhodium, each being present in an amount sufficient to enhance the isomerization activity of said silica-alumina catalyst, the quantity of palladium present in the catalyst exceeding the amount of rhodium.

12. A catalyst consisting essentially of silica-alumina, hydrocarbon-cracking catalyst containing 50–95% by weight of silica and having incorporated therein a co-promoter consisting essentially of 0.05–0.7% by weight of palladium and 0.01–0.2% by weight of rhodium, based on total catalyst composition, the quantity of palladium present in the catalyst exceeding the amount of rhodium.

13. A catalyst consisting essentially of silica-alumina, hydrocarbon-cracking catalyst containing 50–95% by weight of silica and having incorporated therein 0.2–0.6% by weight based on total catalyst composition of a co-promoter consisting essentially of palladium and rhodium, each being present in an amount sufficient to enhance the isomerization activity of said silica-alumina catalyst, and the quantity of palladium present in the catalyst exceeding the amount of rhodium.

14. A catalyst consisting essentially of a silica-alumina, hydrocarbon-cracking catalyst containing about 50–95% by weight of silica and 50–5% by weight of alumina, based on said silica-alumina catalyst, and having incor-

porated therein 0.2–0.6% by weight, based on total catalyst composition, of a co-promoter consisting essentially of palladium and rhodium, the quantity of palladium present in the catalyst exceeding the amount of rhodium, and the quantity of rhodium present being not less than about 0.01%.

References Cited in the file of this patent

UNITED STATES PATENTS

2,076,953	Lacy	Apr. 13, 1937
2,550,531	Ciapetta	Apr. 24, 1951
2,777,805	Lefrancois	Jan. 15, 1957