

Jan. 17, 1961

H. O. FOLKINS ET AL
ISOMERIZATION CATALYST

2,968,632

Filed July 14, 1958

4 Sheets-Sheet 1

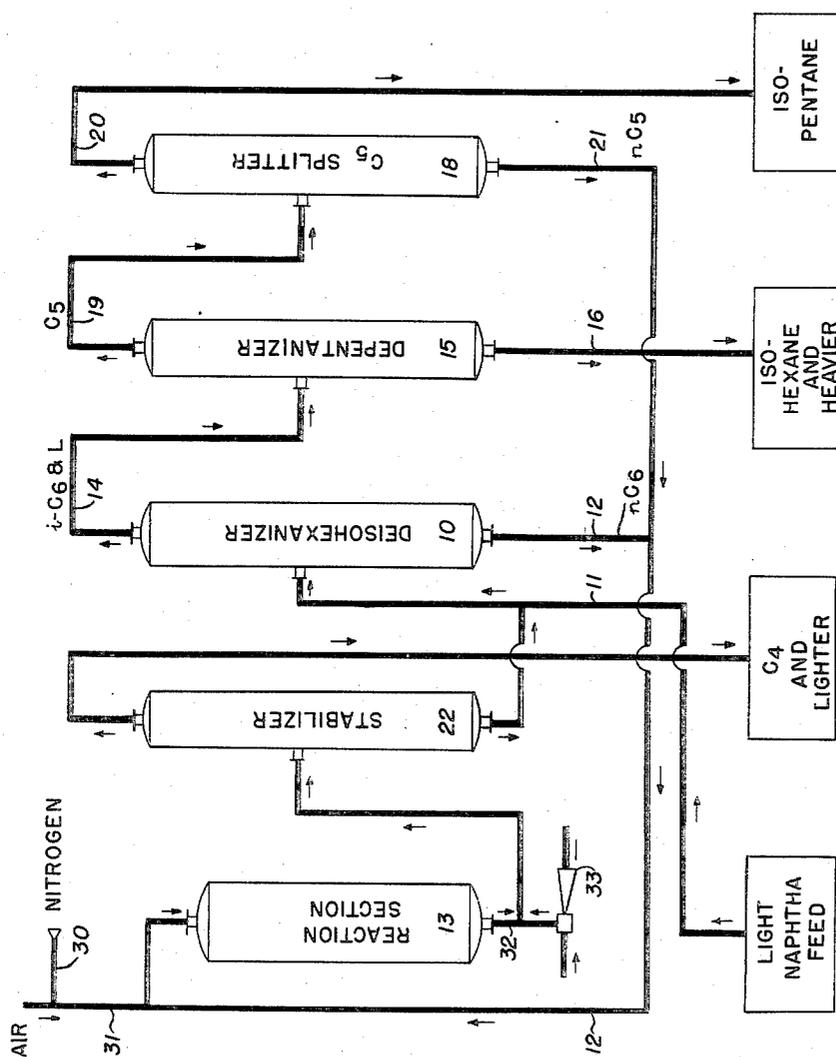


FIG. 1

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4 Sheets-Sheet 2

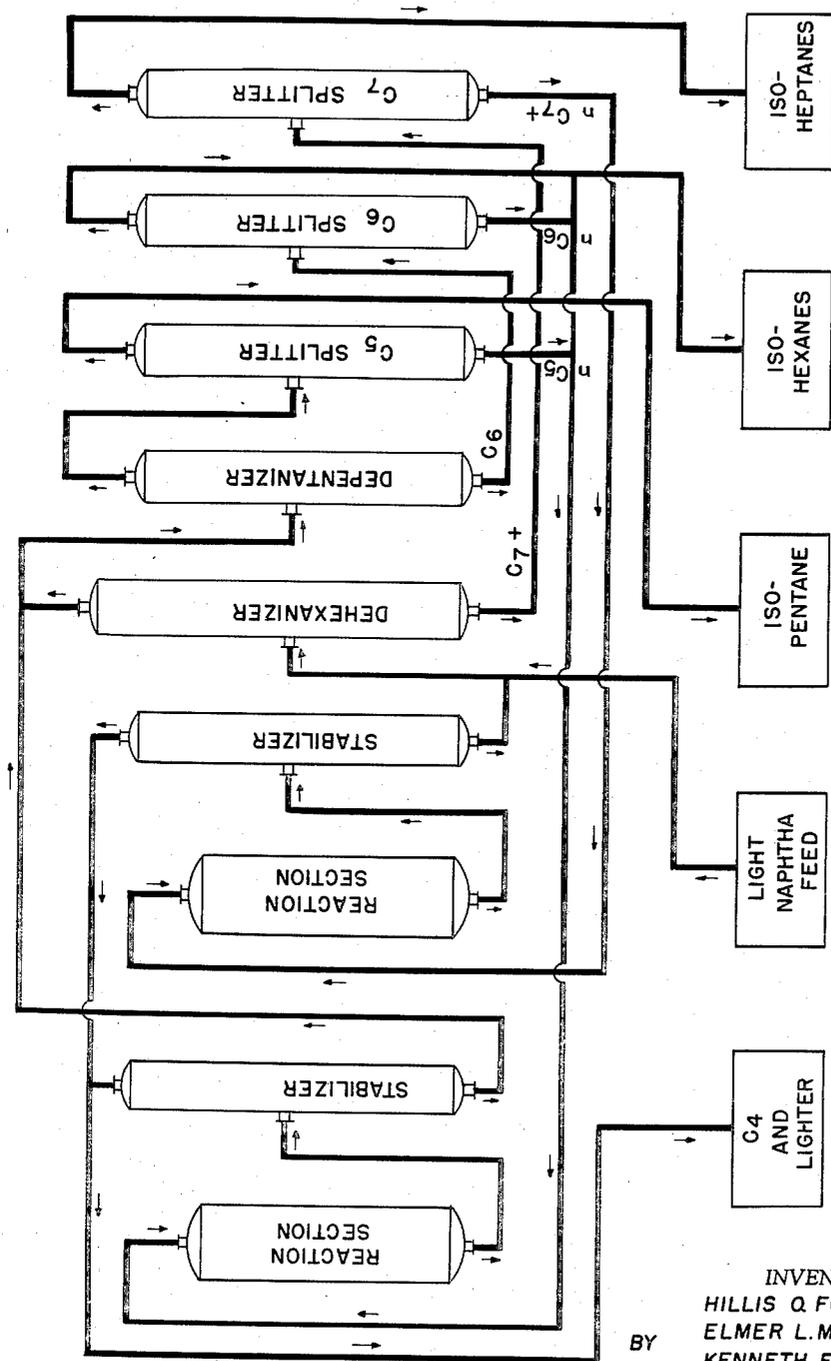


FIG. 2

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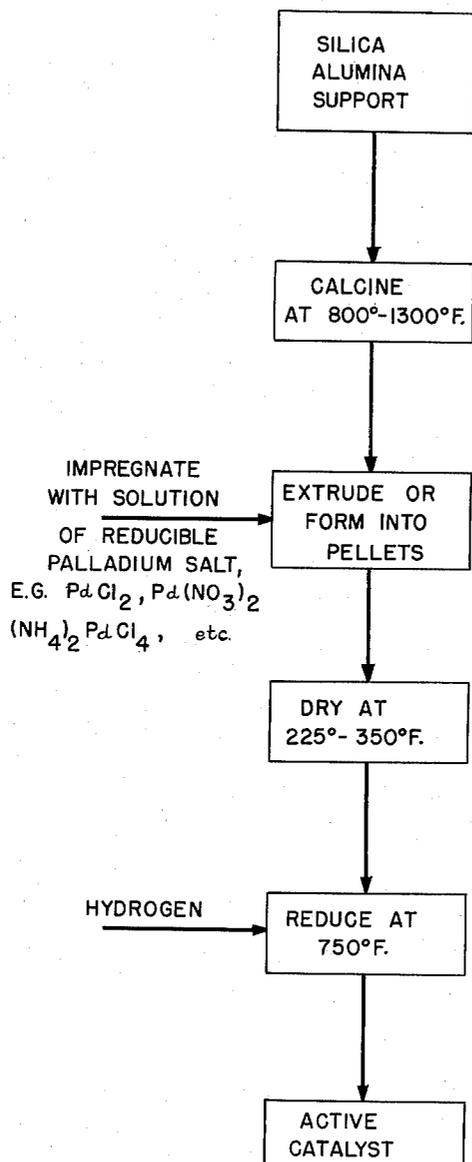
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PREPARATION AND ACTIVATION OF
PALLADIUM ON SILICA-ALUMINA ISOMERIZATION CATALYST

FIG. 3

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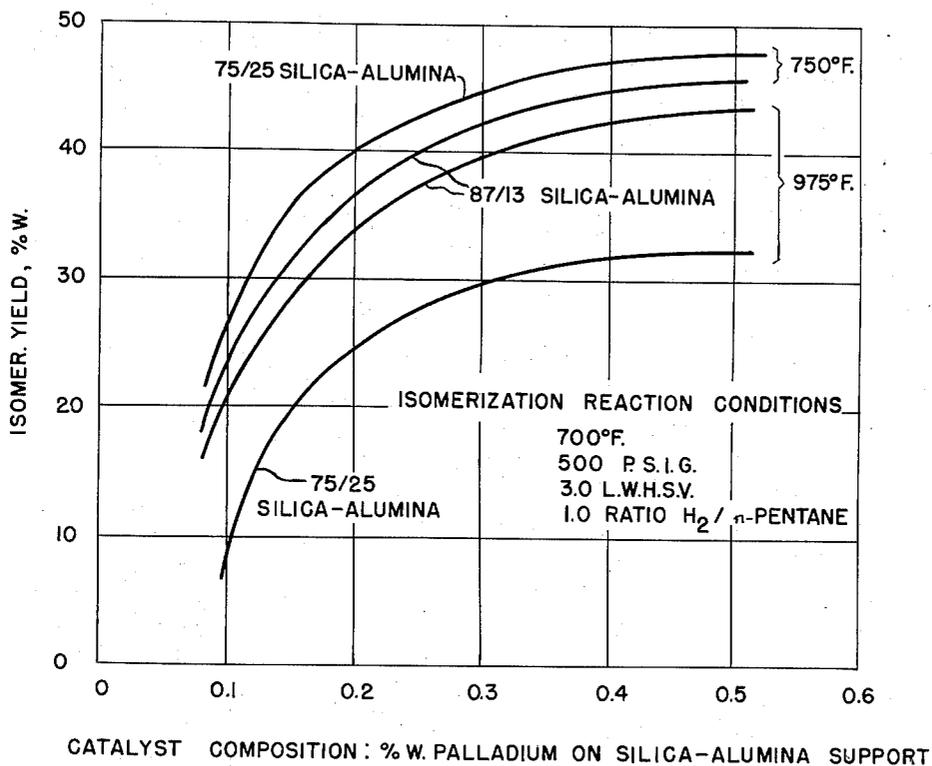
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ISOMERIZATION OF n-PENTANE
EFFECT OF INITIAL REDUCTION TEMPERATURE

FIG. 4

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ISOMERIZATION CATALYST

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Filed July 14, 1958, Ser. No. 748,378

9 Claims. (Cl. 252—455)

This invention relates to the catalytic hydroisomerization of isomerizable hydrocarbons having 4 to 7 carbon atoms per molecule. It is more specifically concerned with an improved method of preparation of a highly active catalyst for 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 aliphatic and alicyclic 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 600 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 palladium-promoted, silica-alumina composite which has been activated in a manner to be described more fully hereinafter.

In integrated petroleum refining operations for the production of high-octane-number gasolines, in order to obtain maximum effectiveness, one of the unit processes selected must be for the processing of feed stocks consisting predominately of the lower-molecular-weight, normally liquid, aliphatic and alicyclic 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 motor 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 in an integrated refining scheme for the production of high-octane-number gasolines, a number of commercial isomerization processes have been developed which utilize solid catalysts. The use of such catalysts eliminates plant corrosion problems and the accompanying high maintenance cost which are attendant upon the use of catalysts of the Friedel-Crafts type. Platinum-promoted catalyst composites such as platinum-halogen-alumina, platinum-silica-alumina, etc., which have been effectively employed in hydroforming operations, have also been utilized in isomerization processes. These catalysts, however, require high operating temperatures which are disadvantageous because isomerization is an equilibrium reaction, the efficiency of which decreases with an increase in the processing temperature. As a result, at the high temperatures employed, the equilibrium product contains substantial quantities of low-octane number paraffins which were 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 cost for carrying out the reaction, and added expense for fabricating process vessels to withstand the combination of high pressures and high tem-

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peratures 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 and thus avoids the disadvantages accompanying high-temperature isomerization using platinum 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 isomerizable, saturated hydrocarbons having 4 to 7 carbon atoms per molecule at temperatures not higher than about 800° F. in the substantial absence of hydrocracking.

It is another object of this invention to provide a low-temperature, highly selective, hydroisomerization process for improving the octane number of petroleum-derived feed stocks consisting essentially of C₅-C₆, normal paraffinic hydrocarbons.

It is an additional object of this invention to carry out the hydroisomerization process employing a solid, non-corrosive catalyst utilizing relatively low temperatures not higher than about 800° F. which permit the substantial production of branched-chain isomerization products with a minimum loss to gaseous products due to hydrocracking, consisting of butanes and lower-molecular-weight hydrocarbons.

It is a further object to provide an improved method of activation of an isomerization catalyst which produces a more active catalyst.

A still further object of this invention is to provide a process of catalyst activation in which a palladium on silica-alumina catalyst is activated by reduction with hydrogen at a temperature of about 750° F. whereby the catalyst is substantially more active in isomerizing hydrocarbons.

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

Figures 1 and 2 are illustrative processing schemes employing the process of this invention.

It has been found that catalysts consisting essentially of small amounts of palladium incorporated in a silica-alumina cracking catalyst, containing not less than about 50% by weight of silica, exhibit high activity and selectivity for the isomerization of saturated, aliphatic and alicyclic, isomerizable hydrocarbons having 4 to 7 carbon atoms per molecule. These catalysts will operate efficiently at reaction temperatures not exceeding about 800° F. However, these catalysts function at highest activity only when activated by reduction with hydrogen at moderately high temperatures, as will be described more fully hereinafter. In carrying out the process of this invention, a composite catalyst containing 0.01-1.0% by weight of palladium, based on total catalyst composition, incorporated in a silica-alumina hydrocarbon cracking catalyst containing more than 50% by weight of silica, based on said cracking catalyst, is employed to carry out the hydroisomerization of aliphatic and alicyclic isomerizable hydrocarbons having 4 to 7 carbon atoms per molecule, employing the following operating conditions:

	Range	Preferred Range
Temperature, ° F., for:		
n-C ₄	700-800	725-800
n-C ₅	680-775	700-780
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 C₄, of limiting reactant fed per hour per unit volume of effective catalyst bed.

In this isomerization process a variety of processing schemes are available. In Figure 1 is shown a simple scheme which utilizes a feed preparation and product recovery 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 residue 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 C₅-splitter 18 through line 19. Isopentane is recovered in the fractionator overhead and sent to storage or transferred to gasoline blending facilities (not shown) through line 20, and the residue consisting predominantly 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 initially treated in stabilizer 22 to separate the butane and lighter products. The pentane-and-heavier fraction is then processed in deisohexanizer as described above.

Catalysts employed in carrying out the process of this invention are initially prepared by conventional techniques by incorporating a small amount of palladium in a hydrocarbon cracking catalyst consisting of a silica-alumina composite containing more than 50% silica. The small amount of palladium is incorporated in the silica-alumina support by impregnation of the support with a solution of a reducible palladium salt, such as the chloride or nitrate, or with a solution of mixed palladium salt such as ammonium chloropalladite. The preparation of the supported catalyst is generally carried out by wetting the support with an aqueous solution of palladium chloride. It may be desirable, in the event a palladium composition which is dissolved only with difficulty in water at room temperature is used, to employ an aqueous solution of an inorganic acid, such as hydrochloric acid as the solvent for the selected palladium impregnant. The normality of the dilute inorganic acid in which the palladium salt is dissolved should be within the range of about 0.1–4 N and preferably within the range of about 0.5–2 N. The quantity of palladium incorporated in the silica-alumina support can vary between about 0.01 and 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 0.75 wt. percent is employed.

Prior to the impregnation of the silica-alumina gel support, it is preferable that this component of the catalyst composition, which has generally been dried in the preparation at an elevated temperature in the range of 300–500° F. to remove any re-adsorbed water from the support, be calcined at a temperature within the range of about 800–1300° F. for a time sufficient to remove the gel water and set the gel structure. When these conditions obtain, the water content of the silica-alumina composite as determined by ignition will be less than about 1.0%. Small amounts of water, however, are retained in order to avoid collapsing the gel structure. In carrying out the calcining step the catalyst is treated, depending upon the temperature used, for about 1 to 8 hours.

After impregnation of the support, the impregnated mass is dried at a temperature within the range of 225–350° F. The "green" catalyst, if in fluid or powdered form, may then be pelleted or formed into suitable size. Alternately, the catalyst support may be pelleted or extruded into suitable shapes before impregnation.

The "green" or dried catalyst mass is then activated by contacting it with a stream of hydrogen for a time sufficient to substantially reduce the palladium component of the "green" catalyst to the metallic state. This reduc-

tion generally can be effected by heating the catalyst mass in hydrogen to decompose and reduce the metal salt to the metallic form. Reduction temperatures are generally in the range of 750°–975° F. While the reduction may be carried out at 975° F. to produce a satisfactory catalyst, we have found that reduction temperatures of 750°–800° F. are much preferred since the catalyst produced by activation at this temperature is much more active. In general, 2000 to 5000 s.c.f. of H₂/bbl. of catalyst are used and this phase of the catalyst preparation is carried out for a period of 2–24 hours. The preferred method of catalyst preparation and activation is shown in a flow diagram in Figure 3.

Although the preparation of supported palladium catalysts employed in the process of this invention is generally carried out in accordance with the foregoing procedure, other manipulative procedures for incorporating the desired amount of metallic palladium on the selected silica-alumina catalyst base can be used, including successive multiple impregnations and techniques of activation wherein a combination of oxidation and reduction steps are used to provide the desired catalyst.

In selecting the silica-alumina hydrocarbon cracking catalyst for use as support 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, this component of the isomerization catalyst composition will have a silica content within the range of about 50–95% by weight, and preferably 75–90%, and an alumina content within the range of about 50–5%, and preferably 25–10%, and will be composited to evince acidic properties and hydrocarbon cracking activity. 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. Suitable procedures for the preparation of silica-alumina supports may be found in "Catalysis" (Emmett), vol. I, p. 341. Reinhold Publishing Co., 1954, and in Industrial and Engineering Chemistry, 44, 2860 (1952). It is also possible to prepare a catalyst which can be employed in the instant invention by contacting silica hydrogel with a solution of an aluminum salt and a palladium salt of the desired concentrations. After drying the mixture, it is heated for a sufficient time to effect the decomposition of the salts. Thereafter the palladium is reduced to the metallic state by treatment with hydrogen at elevated temperatures.

The process of this invention is especially adaptable for effecting the isomerization of feed stocks consisting predominantly of normal pentane and/or normal hexane to produce an octane improvement by promoting the molecular rearrangement of these hydrocarbons, or mixtures containing them, such as light petroleum fractions having an ASTM 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-promoted, silica-alumina composite catalyst in the isomerization of low-boiling isomerizable hydrocarbons having 4 to 7 carbon atoms.

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

Composition:	Weight percent
Al ₂ O ₃ -----	24.4
Na ₂ O -----	0.021
SO ₄ -----	0.25
Fe -----	0.25
SiO ₂ -----	75.3

with an acidified, aqueous solution of palladium chloride. The palladium chloride solution was prepared by dissolving 6.0 grams of palladium chloride dihydrate in 500

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mls. of about 1 normal hydrochloric acid. To prepare a catalyst containing 0.6% by weight (based on total catalyst composition) of palladium on a silica-alumina support consisting normally of 75% by weight of silica and 25% by weight of alumina, 500 grams of the silica-alumina microspheres were placed in a suitable vessel containing 500 mls. of palladium 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 wetted mass was milled thoroughly to effect distribution of the impregnating solution throughout the support. The impregnated support was removed from the vessel, dried at about 230° F. for sixteen hours, and subsequently pelleted into 1/8 x 1/8 inch pellets. Thereafter, the dried mass 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. After purging with N₂ and cooling to 750° F., the catalyst was oxidized with air for one hour. Then when cool, the catalyst was placed in the reactor and heated to

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after which it was cooled to 700° F. Following this, the reactor was pressurized to reaction pressure with hydrogen and the hydrocarbon feed stock was charged under desired conditions.

A tabular summary of data obtained employing the foregoing catalyst composition, as well as other catalyst compositions similarly prepared, is set forth in Table I. Also included in Table I are comparative data demonstrating the superiority of the instant palladium-promoted silica-alumina over similar catalysts employing platinum as the promoting agent.

The advantages that are to be obtained from employing the process of this invention are clearly shown by the data presented in Table I. It is seen that while platinum-promoted catalysts are effective for the isomerization of n-C₅ paraffinic, hydrocarbon-containing feed stocks, in order to obtain high yields of isomers, temperatures above about 825° F. are required, but then the efficiencies are lower. In contradistinction, the use of the palladium-promoted silica-alumina composites in the process of this invention unexpectedly produce better selectivities, conversions, and resultant yields at much lower temperatures.

TABLE I

Catalyst Composition: Promoter, Wt. Percent ¹ Support, Wt. Percent ²	75 SiO ₂ - 25 Al ₂ O ₃		0.6 Pd 75 SiO ₂ -25 Al ₂ O ₃		0.6 Pd 87 SiO ₂ - 13 Al ₂ O ₃	0.4 Pd 87 SiO ₂ - 13 Al ₂ O ₃	0.6 Pt 75 SiO ₂ - 25 Al ₂ O ₃
	Run Conditions:						
Temp., ° F.	737	740	739	740	740	740	739
Pressure, p.s.i.g.	500	700	700	500	500	500	500
L.V.H.S.V.	2.76	1.97	2.07	3.0	3.06	2.94	2.97
H ₂ /HC mol ratio	1.04	20.3	1.93	1.0	0.98	1.02	1.01
Feed, Wt. Percent:							
i-C ₅		1.0	0.7	1.0	1.2	1.2	1.2
n-C ₅		97.0	64.8	97.0	96.7	96.7	96.8
cyclopentane		1.8	1.1	1.8	1.6	1.6	1.7
i-C ₆		0.2	0.4	0.2	0.5	0.5	0.3
n-C ₆			31.8				
methylcyclopentane			1.2				
Product, Wt. Percent:							
C ₁ and lighter		0.8	1.1	1.6	1.6	1.5	1.2
i-C ₃		55.2	34.0	53.7	55.6	54.8	41.1
n-C ₃		41.9	31.0	43.0	39.9	41.6	55.5
cyclopentane		1.5	1.1	1.2	1.7	1.4	1.6
i-C ₆		0.6	22.6	0.5	1.0	0.7	0.6
n-C ₆			9.0				
methylcyclopentane			1.1				
cyclohexane			0.1				
Conversion	6.7	56.8	58.6	55.7	58.7	57.0	42.7
Yield	4.7	55.9	57.5	54.1	56.8	55.4	41.2
Selectivity	69.5	98.4	98.1	97.1	96.8	97.3	96.6

¹ Based on catalyst composition.² Based on support.

975° F. in H₂. Thereafter, the catalyst was treated with 6-8 s.c.f.h. of hydrogen at 975° F. for 8 to 16 hours,

In Table II there is illustrated another feature of the instant invention.

TABLE II

Effect of support

Catalyst Composition: Promoter, Wt. Percent ¹ Support, Wt. Percent ²	0.4 Pd 87 SiO ₂ - 13 Al ₂ O ₃	0.4 Pd 75 SiO ₂ - 25 Al ₂ O ₃	0.4 Pd 71 SiO ₂ - 24 Al ₂ O ₃ - 5 ZrO ₂	0.4 Pd 65 SiO ₂ - 35 MgO	0.2 Pd 75 SiO ₂ - 25 Al ₂ O ₃	0.2 Pd 5 SiO ₂ - 95 Al ₂ O ₃
Run Conditions:						
Temp., ° F.	700	700	700	700	700	700
Pressure, p.s.i.g.	500	500	500	500	500	500
L.V.H.S.V.	3.0	3.0	3.0	3.0	3.0	3.0
H ₂ /Hydrocarbon mol ratio	1.0	1.0	1.0	1.0	1.0	1.0
Feed, Wt. Percent:						
i-C ₅	1.3	1.3	1.3	1.3	1.3	1.3
n-C ₅	97.0	97.0	97.0	97.0	97.0	97.0
Cyclopentane	1.6	1.6	1.6	1.6	1.6	1.6
i-C ₆	0.2	0.2	0.2	0.2	0.2	0.2
Conversion	43.6	38.5	23.1	0.3	31.5	5.2
Yield	42.9	37.3	22.6	0.3	31.1	4.8
Selectivity	98.5	97.0	98.0	95.0	98.7	93.0

¹ Based on catalyst composition.² Based on support.

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-containing catalyst is deleteriously affected. It is seen also that the type of acidic support is important if high isomerization activity is to be attained. Thus, a catalyst composed of palladium on a support consisting of a commercial, acidic, silica-magnesia, cracking catalyst showed negligible isomerization activity.

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 immediately ahead of the reactor to effect the removal of the sulfur compounds from the feed. The guard case is at substantially the same total flow and operating conditions, except for temperature, employed in the isomerization. Preferably, the pretreatment should be effected by 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 and in the vapor phase, are briefly described by Kalichevsky, *Petroleum Refiner*, vol. 30 (4) at page 117, et seq. In addition to sulfur removal, the "guard case" serves to remove trace metal contaminants, and saturate any olefins which are present. When the guard "catalyst," is saturated with sulfur, i.e., when a significant amount of sulfur breaks through into the effluent, it is bypassed and prepared for regeneration or removal of sulfur by high-temperature oxidation in the presence of a steam-carrier gas. The process need not be interrupted or shut-down, provided the sulfur content of the feed is less than about 3 p.p.m. This is about the maximum level normally expected in the raw feed to the "guard case" unit. The regeneration of the "guard case" is carried out in the same manner as that for hydrodesulfurization reactors. A small furnace is needed for the steam preheat. The final oxidation temperature should be about 1000° F. After gross sulfur removal is complete, steam and air are removed from the vessel by evacuation and/or purging. The unit is then returned to normal processing conditions. The operating temperature of the "guard case" can be from about 550° to 725° F. Employing temperatures substantially higher than 725° F. causes excessive hydrocracking. The amount of guard catalyst employed will depend upon the following factors: (1) the amount of sulfur in the feed to this unit, (2) the length of the processing cycle between regenerations of the guard case, and (3) the total flow rate. The amount of sulfur that the guard will hold is calculated on the assumption that one atom of sulfur is held by one atom of metal. The efficiency factor to be used with this relation should be in the range of 70 to 90%.

It is also preferred that the hydrogen employed as a processing aid in the hydroisomerization process be substantially free of H₂O, O₂, CO, H₂S, 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 hydrogen employed can be obtained from conventional sources. Commercial isomerization systems, however, will for reasons of convenience and efficiency operate in conjunction with conventional hydroforming units. In these instances the hydrogen-rich gas from the hydroformer can be employed not only for make-up in the isomerization reaction section, but also for putting the unit on stream.

Although the small quantities of dry hydrocarbons in this hydrogen-rich stream will result in a small loss in yield at the same space velocity, if the yield is to be held constant, the change can be compensated for by an appropriate change in space velocity.

In the preparation and activation of the catalyst we investigated the effect of variations in the temperature of the hydrogen reduction step on the isoparaffin yield from the activated catalyst. Unexpectedly, we found that when the activation of the catalyst by hydrogen reduction is carried out at 750°–800° F. a much more active catalyst is obtained than when the reduction is carried out at 975° F. The difference in activity is greater for the 75/25 silica-alumina base than for 87/13 silica-alumina. However, the difference is substantial and exists at all proportions of palladium on the catalyst. A number of experiments were carried out using 75/25 and 87/13 silica-alumina supports with different proportions of palladium deposited thereon. The palladium was deposited in the manner described above in the principal example. Some of the catalysts were reduced with hydrogen at 975° F. and some reduced at 750° F. The catalysts thus activated were used in the isomerization of n-pentane at 700° F., 500 p.s.i.g., liquid weight hourly space velocity of 3.0, and hydrogen/n-pentane ratio of 1.0. The isopentane yields from these catalysts are compared in Figure 4. Thus, comparing a catalyst consisting of 0.12% Pd on 75/25 silica-alumina it is seen that the catalyst activated by reduction at 975° F. produced an isopentane yield of 14% while the same catalyst composition activated at 750° F. produced an isopentane yield of 31%. As shown by the curves in Figure 4 this difference holds for higher concentrations of palladium and for different support compositions. A catalyst consisting of 0.48% Pd on 75/25 silica-alumina which was activated by reduction of 975° F. produced an isopentane yield of 33% while the same catalyst composition activated at 750° F. produced an isopentane yield of 48%. After three regenerations at temperatures ranging from 750° to 975° F., the latter catalyst showed some decrease in activity, but still produced a yield of isopentane of 41%, well above the 33% yield produced with the catalyst initially activated at 975° F. Thus it is seen that the method of activation of this invention produces a lasting improvement in activity. Similarly, a catalyst consisting of 0.48% Pd on 87/13 silica-alumina which was activated at 975° F. produced an isopentane yield of 43.1% while the same catalyst composition activated at 750° F. produced an isopentane yield of 45.7%.

The operating conditions for the catalyst-reactant systems are normally selected so that degeneration or fouling does not occur. However, degeneration may develop from extremely long process periods or operational upsets. Operational upsets involving reactor temperatures in excess of the design level and/or the loss of hydrogen circulation can cause catalyst fouling. In these cases, a simple regeneration in place is accomplished by the procedure given subsequently. Operating temperature and regeneration temperatures are so low for the refractory catalyst that virtually no aging or sintering occurs to cause deactivation. No deactivation has been encountered even in accelerated aging (during regeneration) tests of 150° to 200° F. higher temperatures than those recommended. The function of the regeneration is the revivification of a lower-activity catalyst to one equivalent to its virgin activity. Aside from poisons like arsenic, and allowing for the gross removal of sulfur in the hydrosulfurization system and in the isomerization guard-case, only two fundamental factors cause temporary activity loss. They are coke deposition, encountered only by misoperation or by exhaustive processing, and certain combinations of water-vapor partial pressure in relation to temperature. The presence of trace water, in excess of that likely from saturated feed streams at roughly 90° F., has no effect

during processing conditions. However, high partial pressures of water vapor, high temperature, and extended times at certain combinations of these cause the catalyst to become temporarily deactivated. These conditions should not be employed in the regeneration cycles. In the event difficulties arise, proper definition of procedure is needed. A simple regeneration cycle of the type defined herein will completely revive a catalyst which has lost activity due to the said problem. To define typical instances to be avoided, the following examples are given:

(1) If treatment gases are dry, which means less than about 1 mm. (mercury) partial pressure of water, the catalyst can withstand temperatures as high as 975° F. for extended times and up to 1000° F. for times less than about one hour.

(2) If the gases in the reactors contain 15 mm. (mercury) partial pressure of water, then the upper limit of temperature and time is 975° F. for about one hour.

(3) A partial pressure of 25 mm. or greater at 975° F. or higher cannot be tolerated.

Another operational situation causes catalyst fouling and results in the need for catalyst regeneration. If the reactor is depressurized after a processing cycle, it is advisable that the simple regeneration be conducted. Apparently, coke lay-down is unavoidable when the reactor is depressurized for any reason.

It is emphasized that these conditions which cause difficulty are out of the ordinary, and can be avoided by proper design and operation of the reaction section.

The three functional variables involved in the regeneration are as follows:

(1) *Condition of dryness of the catalyst during all regenerative treatments.*—This is controlled by the water partial pressure and temperature within the reactor. The water partial pressure within the catalyst bed should be as low as practicable and certainly below 15 mm. mercury.

(2) *Oxidation temperature.*—The safe upper level of temperature is 950° F. Below this value and above about 700° F., the oxidation temperature is not critical, except that it should be high enough for substantial coke oxidation. A burning front temperature of about 800°–850° F. and a final treatment with the inlet gas and entire bed at about 850° F. are recommended. The time requirement is consistent with oxidation completion and manipulations. Normally, the coke laid down will be only about 0.1 to 1% of the catalyst at the metal content employed in the catalyst. The metal will completely oxidize with the oxygen partial pressure at any convenient level, e.g., 1–5% oxygen at 25 p.s.i.g. total pressure. The inert gas can be nitrogen, or carbon monoxide-free flue gas.

(3) *Reduction temperature.*—The safe upper level of reduction temperature is 950° F. The recommended reduction temperature is about 750°–800° F. The reduction gas can be pure hydrogen or reformer off-gas. The water partial pressure during reduction should be below about 15 mm. and preferably as dry as practicable. A reduction time sufficient to reduce the reducible constituents of the catalyst components is employed. Generally a time of about one hour at these conditions is recommended. It is also suggested that in the initial phase of the reduction, when water is liberated from the reduction of the oxide, the total pressure and the circulation gas rate should be such that low water partial pressure exists in the catalyst bed at all times.

Other techniques can be employed in the design of the regeneration system. For example, first, reverse flow can be used in the reactor for purging, or evacuation, and for the initial burn. Since it is desirable to eliminate sulfur compounds and water from the gases and the catalyst, the dry oxidation-gas flow should be once-through and not recycled. The oxidation time and capacity are so low that this should be the easiest and best approach. Second, if an inert gas generator is employed, this gas should be dried in order to avoid possible difficulty from water and to afford a means of drying the catalyst by purging.

Third, regeneration connections to and around the reactor should include a minimum utilization of piping and equipment normally used for the feed and product streams. If the recycle gas compressor is to be employed during the regeneration, processing tanks, exchangers and process piping should be by-passed.

A catalyst regeneration employed after a long processing cycle, can be carried out as follows:

(1) After the feed system has been shut down and the heat outputs have been decreased, the gas recycle circulation is continued until the feed lines and reactor are essentially purged of wet hydrocarbons at operating temperature and pressure. Gas circulation is then stopped.

(2) The complete unit is depressurized and the gas vented.

(3) After appropriate valving changes, the isolated reactor is dried or purged with dry, inert gas. Evacuation, as a method of drying and eliminating combustibles, can be substituted for the initial inert gas purge. The catalyst bed temperature is maintained around 750°–800° F. for the purging step.

(4) After the purging step and the combustible gas removal have been completed, the oxidation step is commenced. When the bed and inlet gas temperatures are in the range 750°–800° F., air (oxygen) is introduced into the carrier gas to a content of about 1 to 5% oxygen. The mass rate of oxygen is controlled so that oxidation front temperatures do not exceed 850° F. When the initial burn is complete, the reactor temperature is lined out at about 850° F. in the presence of the oxygen-containing gas for a time consistent with thorough oxidation. At this time and hereafter, the presence of some moisture in the regeneration gases is not critical, except that water partial pressures should be held below about 15 mm.

(5) After the removal of oxygen from the reactor and system, the catalyst is reduced with hydrogen or hydrogen-rich gas at 750°–800° F., at about one atmosphere and for a time period of about one hour. This concludes the regeneration cycle and the unit is pressurized, hydrogen circulation is established, and the bed temperature is adjusted to the defined level for processing conditions.

Referring to Figure 1, reactivation of the catalyst is provided for by means of the reactivation system shown schematically. Inert purging gas, such as nitrogen from line 30, is fed into line 31 through which air is admitted into the system. Before initiating regeneration, the reaction system is thoroughly purged of hydrocarbons. Thereafter, the reaction system is depressurized to about atmospheric pressure and the system 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 activated catalyst. This is followed by the reduction step above-described. Then the reactor is cooled to the desired reaction temperature, the reaction system is repressured, and fresh feed is reintroduced 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 for the processing of light hydrocarbon feed stocks. For example, an alternative processing scheme is shown in Figure 2. The process of this invention finds application in combination with other conventional, unit-refining processes, such as reforming, or with 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. In applications of this nature, the debutanized, light, straight-run gasoline is deheptanized, either in existing equipment, such as a Catalytic Reformer feed preparation unit, or in new equipment. The C₅-C₆ fraction is then split, and the C₅'s, including debutanized C₅ reactor effluent, are split to produce an isopentane product and a normal-pentane reactor feed. The degree of fractionation determines the product octane number, since normal pentane is recycled to extinction.

In the alternative, the C₆ fraction can be employed in gasoline blending, or can be isomerized by one of two methods. Hexane fractions high in normal hexane content can be improved considerably by direct single-pass isomerization. Further improvement in octane number is possible by first splitting the iso- from the normal hexane, and then isomerizing the normal hexane fraction. Further octane improvement is possible by recycling normal hexane to extinction. This, however, would require an extra fractionation step to prevent an excessive build-up of methyl cyclopentane in the recycle stream.

An alternate method for processing normal pentane and the total hexane fraction in a single reactor involves deheptanizing a debutanized feed stock. The deheptanized feed is deisopentanized, and the resultant stream passed through the reaction system. The debutanized reactor effluent then is fractionated to produce an isomerized hexane fraction, and a pentane recycle stream which passes to the deisopentanizer. In this alternate processing, reaction conditions are determined by the more reactive hexanes, resulting in a lower conversion per pass of normal pentane. The greater fractionation cost must be balanced by the decreased reactor section costs, since only one reaction section is required. In processing mixed feed stocks, it is evident that optimum operating conditions should be selected depending upon the admixture employed. These conditions are defined as those which allow the catalyst to operate at its highest activity consistent with no decline in activity with processing time, and in the substantial absence of hydrocracking. The factors which determine the reaction rate for a given catalyst-reactant system are: (1) temperature of reaction, (2) reactant inlet partial pressure, (3) hydrogen partial pressure and (4) the partial pressure of inert diluents. For example, Table III defines operating conditions which have been determined for several feed stocks.

TABLE III

Feed Description	Temp., ° F.	Total Press., p.s.i.g.	H ₂ /Hc Mole Ratio	LVHSV
80% n-hexane—20% cyclohexane	725	645	3.2	2.8
60% n-pentane—30% n-hexane—10% cyclohexane	725	700	2	2
60% n-pentane—30% n-hexane—10% cyclohexane diluted with 5% h-heptane	725	700	2	2

This application is a continuation-in-part of our co-pending application, Serial No. 691,996, filed October 23, 1957.

What is claimed is:

1. A method of preparing a highly active isomerization catalyst which comprises impregnating a precalcined silica-alumina support, containing at least 50 wt. percent silica, with a sufficient amount of a solution of a reducible palladium compound to produce a palladium concentration of 0.01–1.0 wt. percent on the support, drying the impregnated catalyst, and activating the catalyst by reduction with hydrogen at a temperature of about 750°–800° F.
2. A method according to claim 1 in which the reducible palladium compound is of the group consisting of palladium chloride, palladium nitrate, and ammonium chloropalladite.
3. A method according to claim 2 in which the catalyst is reduced with 2000–5000 s.c.f. of hydrogen per barrel of catalyst for a period of 2–24 hours.
4. A method in accordance with claim 2 in which the catalyst is formed into pellets after impregnation with the palladium compound solution and prior to drying.
5. A method of preparing a highly active isomerization catalyst which comprises calcining a silica-alumina gel, containing at least 50 wt. percent silica on a dry weight basis, at a temperature of about 800°–1300° F. for a time sufficient to remove the gel water and set the gel structure, impregnating the calcined silica-alumina with a sufficient amount of a solution of a reducible palladium compound to produce a palladium concentration of 0.01–1.0 wt. percent, drying the impregnated catalyst at 225°–350° F., and activating the catalyst by reduction with hydrogen at 750°–800° F.
6. A method in accordance with claim 5 in which the catalyst is formed into pellets after impregnation with the palladium compound solution and prior to drying.
7. A method according to claim 5 in which the reducible palladium compound is of the group consisting of palladium chloride, palladium nitrate, and ammonium chloropalladite.
8. A method according to claim 5 in which the catalyst is reduced with 2000–5000 s.c.f. of hydrogen per barrel of catalyst for a period of 2–24 hours.
9. A highly active isomerization catalyst produced in accordance with the process of claim 5.

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