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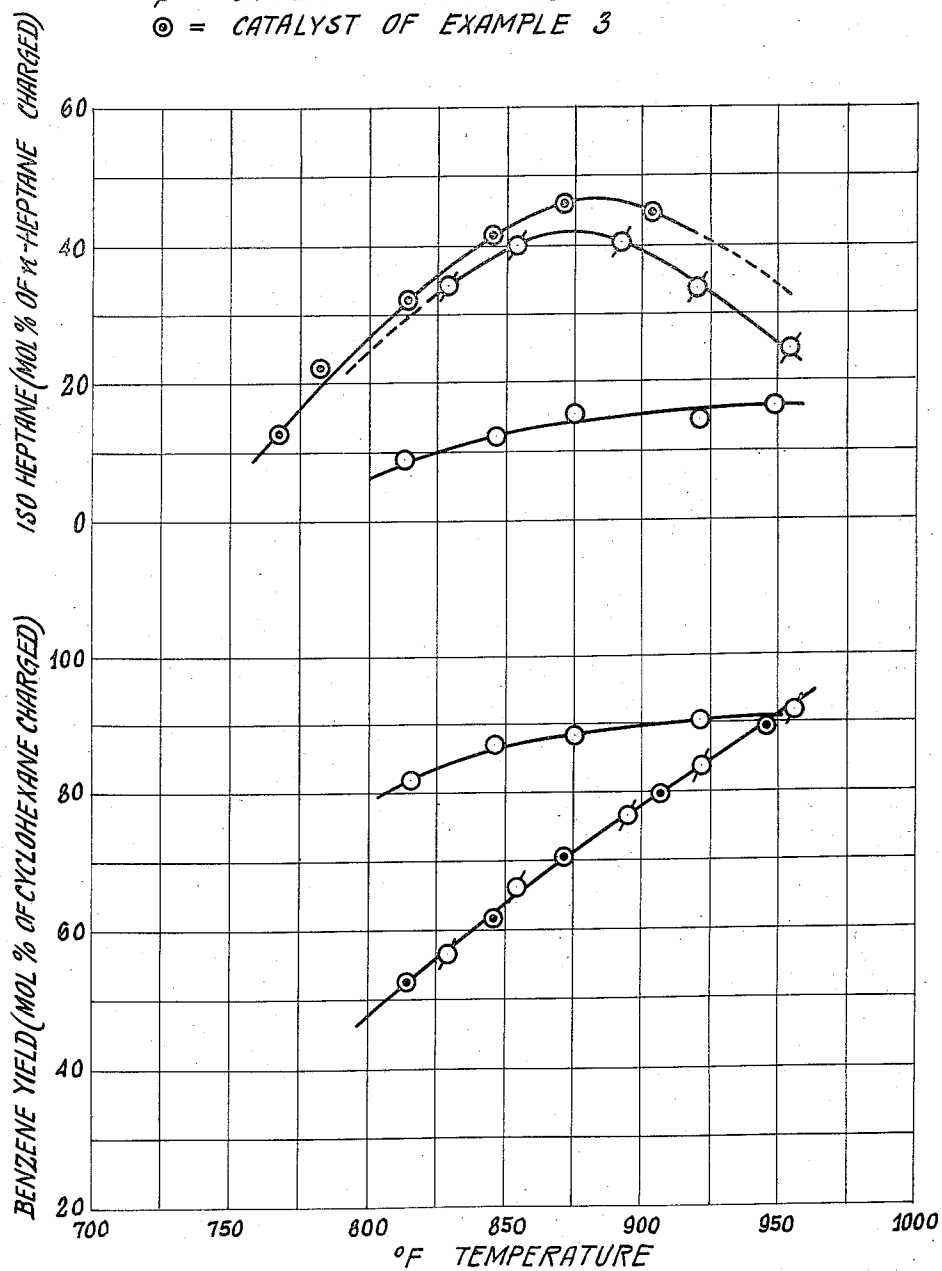
P. B. WEISZ

2,854,403

CATALYTIC REFORMING

Filed July 26, 1954

○ = CATALYST OF EXAMPLE 1
◊ = CATALYST OF EXAMPLE 2
⊙ = CATALYST OF EXAMPLE 3



INVENTOR

Paul B. Weisz

BY

Raymond W. Barclay

ATTORNEY

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2,854,403

CATALYTIC REFORMING

Paul B. Weisz, Pitman, N. J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

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This invention relates to an improved catalytic reforming process for obtaining gasoline of high octane number. More particularly, the present invention is directed to catalytic reforming carried out in the presence of a catalyst consisting essentially of a particularly defined mixture of (1) particles of a porous inert carrier impregnated with a small amount of a metal of the platinum series and (2) particles of an acidic cracking component. The invention is further directed to the aforesaid catalyst.

Reforming operations, wherein hydrocarbon fractions such as naphthas, gasolines and kerosene are treated to improve the anti-knock characteristics thereof are well known in the petroleum industry. These fractions are composed predominately of normal and slightly branched paraffinic hydrocarbons and naphthenic hydrocarbons together with small amounts of aromatic hydrocarbons. During reforming a multitude of reactions take place including isomerization, aromatization, dehydrogenation, cyclization, etc. to yield a product having an increased content of aromatics and highly-branched paraffins. Thus, in reforming, it is desired to dehydrogenate the naphthenic hydrocarbons to produce aromatics, to cyclize the straight chain paraffinic hydrocarbons to form aromatics, to isomerize the normal and slightly branched paraffins to yield highly branched chain paraffins and to effect a controlled type of cracking which is selective both in quality and quantity.

Normal and slightly branched chain paraffinic hydrocarbons of the type contained in the above fractions have relatively low octane ratings. Highly branched-chain paraffinic hydrocarbons, on the other hand, are characterized by high octane ratings. Accordingly, one objective of reforming is to effect isomerization of the normal and slightly branched-chain paraffins to more highly branched-chain paraffins. Since aromatic hydrocarbons have much higher octane ratings than naphthenic hydrocarbons, it is also an objective of reforming to simultaneously produce aromatics in good yield. The production of aromatic hydrocarbons during reforming is effected by dehydrogenation of the naphthenic hydrocarbons and dehydrocyclization of the paraffinic hydrocarbons. Aromatic hydrocarbons are also produced by isomerization of alkyl cyclopentanes to cyclohexanes which thereafter undergo dehydrogenation to form the desired aromatics.

Controlled or selective cracking is highly desirable during reforming since such will result in a product of improved anti-knock characteristics. As a general rule, the lower molecular weight hydrocarbons exhibit a higher octane number, and a gasoline product of lower average molecular weight will usually have a higher octane number. The splitting or cracking of carbon to carbon linkages must, however, be selective and should be such as not to result in substantial decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons. The selective cracking desired ordinarily involves removal of one or more lower alkyl groups such as methyl or ethyl from a given molecule in the form of methane or ethane.

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Thus, during reforming, it is contemplated that heptane may be converted to hexane, nonane to octane or heptane, etc. Uncontrolled cracking, on the other hand, would result in decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons. For example, non-selective cracking of normal octane would ultimately lead to eight molecules of methane. Since methane, ethane, and propane cannot be used in gasoline, they constitute a loss in the process and the production of excessive amounts of these lower paraffins accordingly is to be avoided. Butanes, on the other hand, tend to increase the octane rating of gasoline but the effective amount of butane present in the finished gasoline is limited by the maximum permissible vapor pressure.

Uncontrolled cracking, moreover, generally results in rapid formation and deposition on the catalyst of large quantities of a carbonaceous material generally referred to as "coke." The production of coke not only results in decreased yields of gasoline but the deposition thereof on the catalyst surface diminishes or destroys its catalyzing effect and results in shorter processing periods with the accompanying necessity of frequent regeneration by burning the coke therefrom. In those instances where the activity of the catalyst is destroyed, it is necessary to shut down the unit, remove the deactivated catalyst, and replace it with new catalyst. Such practice obviously is time-consuming and inefficient, imparting a greater overall expense to the reforming operation.

When reforming is carried out in the presence of hydrogen under pressure, the formation of coke is to some extent inhibited. Accordingly, it has been general practice to effect reforming in the presence of hydrogen and such processes have sometimes been referred to as hydroforming. An increase in hydrogen pressure during reforming results in increasing the temperature at which aromatization, including dehydrogenation and dehydrocyclization, occurs. The isomerization reactions taking place, on the other hand, are independent of pressure. Reforming in the presence of a catalyst which provides maximum isomerization at relatively low temperatures is disadvantageous in operations wherein pressure conditions have elevated the temperature range of the aromatization reaction. To achieve maximum conversion to high octane gasoline, maximum isomerization should occur at temperatures sufficiently high to effect good conversion to aromatic hydrocarbons.

Accordingly, the choice of catalyst for promoting reforming of hydrocarbons to gasolines of enhanced octane rating is dependent on several factors. Such catalyst should desirably be capable of effecting reforming in a controlled and selective manner as discussed above to yield a product of improved anti-knock characteristics. The catalyst selected should, further, be resistant to poisoning and should also desirably be characterized by high stability and be capable of easy regeneration. The method for preparing such catalyst should be commercially attractive, requiring a minimum of equipment and processing stages.

In accordance with the present invention, a catalyst of the above-defined characteristics has been discovered. Broadly, the present invention provides a reforming catalyst consisting essentially of a mechanical mixture of finely divided particles of a porous inert carrier having deposited thereon a small amount of one or more of the platinum metals, i. e. platinum, palladium, rhodium, osmium, iridium and ruthenium and finely divided particles of an acidic cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} (a) \quad & n \times A. I. = 2 \text{ to } 30 \\ (b) \quad & m \times C_m \times d_s = .1 \text{ to } .8 \end{aligned}$$

where n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with a platinum metal in the mixture, A. I. is the activity index of the acid cracking component, C_m is the platinum metal content expressed in weight percent of the inert carrier, and d_s is the density of inert carrier particles in grams per cubic centimeter. The instant invention also provides a process for reforming hydrocarbon fractions boiling in the gasoline range by contacting them with the above catalyst in the presence of hydrogen under reforming conditions.

It has heretofore been proposed to reform hydrocarbon fractions by subjecting the same under reforming conditions with a catalyst comprising a platinum metal supported on an active cracking component. Thus, it has been taught that a platinum metal deposited on a carrier or support which is inert as regards cracking activity is not an active catalyst for reforming operations.

The cracking activity of a material is conventionally expressed in terms of the percent by volume of a standard hydrocarbon charge which is cracked under specific conditions in the CAT-A test. The method of this test is described in National Petroleum News, 36, page P. R.-N537 (August 2, 1944) and the cracking activity so determined is referred to as the "Activity Index" (A. I.). Accordingly, it will be understood that the term "activity index" when employed in the present specification and claims shall refer to the cracking activity of the material under consideration determined in accordance with the CAT-A method.

In accordance with the process described herein, it has been found, contrary to the teachings of the prior art, that excellent reforming can be achieved when the reforming operation is carried out in the presence of a catalyst consisting essentially of a mechanical mixture of finely divided particles of components having the characteristics defined hereinabove. It has been discovered that hydrocarbon fractions having low octane ratings can be converted into hydrocarbon fractions having high octane ratings, in good yields, by subjecting them to reforming in the presence of hydrogen and a catalyst of the aforesaid character.

The mechanical mixture comprising the present catalyst allows a wide choice for the carrier supporting the platinum metal component. Thus, it is contemplated that the carrier employed herein may be any porous inert material which is not adversely affected by the temperature conditions of reforming. The carrier desirably has a surface area greater than about 10 square meters per gram and preferably in excess of 30 square meters per gram and may extend up to 500 square meters per gram or more. The term "surface area" as used herein designates the surface area of the carrier as determined by the adsorption of nitrogen according to the method of Brunauer et al., Journal American Chemical Society 60, 309 et seq. (1938). The carrier is inert, that is, it is devoid of or exerts negligible catalytic activity under the reaction conditions of reforming discussed hereinbelow. Suitable carriers include single oxides of the metals of groups II-A, III-B, IV-A, and IV-B of the periodic table. Non-limiting examples thereof include alumina, zirconia, titania, silica, magnesia, etc. Other suitable inert materials include charcoal, kieselguhr, porous glass, porcelain, pumice, coke, activated carbon, bauxite, inert earths, etc. The density of the carrier employed, i. e. the bulk density thereof, will usually be within the range of .2 to 2.0 grams/cc. and more particularly between about .4 and about 1.2 grams/cc.

The porous inert carrier serves as a support for a catalytically effective amount of a platinum metal, i. e. platinum, palladium, rhodium, osmium, iridium and ruthenium as well as alloys of the metals. Of the foregoing, platinum and palladium and in particular platinum, are accorded preference. The amount of the platinum metal

contained in the instant catalyst is generally between about 0.05 and about 5 percent by weight of the carrier and more particularly between about 0.1 and about 2 percent by weight of the carrier.

In accordance with the present invention, the weight fraction of inert carrier supporting the platinum metal component may vary widely thereby affording desirable flexibility in the catalyst composition which may be varied with the specific charge stock undergoing treatment and with the particular reaction conditions under which the reforming operation is effected. In general, however, the weight fraction of carrier supporting the platinum metal component of the instant catalyst is between about .1 and about .9.

It is to be understood that following the teachings of this invention, the weight fraction of carrier supporting the platinum metal component, the density of said carrier and the concentration of said metal are so related that the product thereof lies within the range of .1 to .8, thereby fulfilling the condition:

$$m \times C_m \times d_s = .1 \text{ to } .8$$

where m , C_m and d_s have the above-designated significance.

The nature and amount of the acidic cracking component contained in the instant catalyst may, in accordance with the present invention, vary widely. Typical acidic cracking components include synthetic composites of two or more refractory oxides. Generally this group includes oxides of elements of groups II-A, III-B, IV-A and IV-B of the periodic table. Non-limiting examples of the synthetically produced composites include silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-alumina-thoria, silica-magnesia, silica-alumina-magnesia, alumina-boria and the like. In some instances, the above composites may be promoted with small amounts of other metal oxides. The preferred cracking component is a synthetic composite of silica and alumina containing from about 0.25 percent up to about 20 percent by weight of alumina. The activity index of the cracking component employed should desirably be within the range of 3 to 30 but may be outside this range providing the conditions of the expression:

$$n \times \text{A.I.} = 2 \text{ to } 30$$

are fulfilled where A.I. is the activity index of the cracking component and n represents the weight fraction of this component in the catalyst mixture. The latter weight fraction may also vary widely depending on the particular stock undergoing reforming and the specific conditions under which reforming is effected. In general, however, the weight fraction of the acidic cracking component of the instant catalyst is between about .1 and about .9. It is particularly preferred that the acidic cracking component of the present catalyst be characterized by the expression:

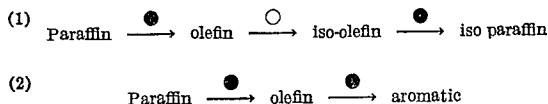
$$n \times \text{A.I.} = 10 \text{ to } 25$$

The particle size of the components comprising the catalyst mixture of this invention has been found to be a critical feature thereof. It has been established, as will be evident from data set forth hereinbelow, that for optimum reforming with the described catalyst, the average particle size of each of the components making up said catalyst should be less than about 100 microns. Excellent results have been obtained with a catalyst having a particle size in the range of about 100 to about 400 mesh (Tyler). It is accordingly contemplated that the catalysts of this invention will in general comprise particles having a diameter below 100 microns and particularly a diameter in the approximate range of 1 to 100 microns.

Without being limited by any theory, it is believed that the optimum results achieved herein with finely divided particles are due to the accomplishment of the two reactions important in reforming, namely isomerization and

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aromatization, by way of olefinic intermediates in accordance with the following reaction steps:



It is believed that each reaction step marked by $\bullet$ takes place on a dehydrogenation center, such as a platinum metal, while each step marked $\circ$ takes place on an acid cracking catalyst center. It is postulated that the two components comprising the instant catalyst mixture, i. e. particles of the platinum metal deposited on an inert carrier and particles of the acid cracking catalyst should present sufficient reaction surface and be sufficiently proximate to one another that the olefinic intermediates formed during the reaction proceed to the desired isomerized or aromatized end-products during the life-time of such intermediates. In accordance with the present invention, it has been discovered that optimum reforming is attained when the particle size of the components making up the instant catalyst is fairly small and specifically less than about 100 microns in diameter.

The catalyst of this invention may be used in the form of discrete particles having the aforesaid requisite diameter or the components having such particle size may be admixed and pelleted, casted, molded, or otherwise formed into pieces of desired size and shape such as rods, spheres, pellets, etc., it being essential, however, that each of said pieces is composed of particles of both components having a particle diameter of less than about 100 microns.

The process of this invention can be carried out in any equipment suitable for catalytic operations. The process may be operated batchwise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the process is adapted to operations using a fixed bed of catalyst. Also, the process can be operated using a moving bed of catalyst wherein the hydrocarbon flow may be concurrent or countercurrent to the catalyst flow. A fluid type of operation wherein the catalyst is carried in suspension in the hydrocarbon charge is well adapted for use with the instant catalyst since pelleting or otherwise shaping of the catalyst components is thus rendered unnecessary.

The carriers for the platinum metal component of the instant catalyst, as indicated hereinabove, are inert with respect to reforming of hydrocarbons, i. e. they are not effective in catalytic reforming operations, under the conditions of the process of this invention. A number of platinum-containing reforming catalysts have heretofore been proposed wherein the platinum metal is impregnated on an alumina base. Such base has been known to impart stability to the platinum in subsequent aging thereby permitting use of the catalyst over an extended period of time in reforming operations without necessitating regeneration. However, inasmuch as the alumina base itself is not acidic, it has heretofore been the practice to combine the alumina with promoting agents, such as halogens, boria, and the like. It is well known that such promoters are not permanent but may be lost upon contact with water vapor which is inherently or accidentally contained in the hydrocarbon feed stock.

Utilizing one embodiment of this invention, it is now possible to combine the advantages of employing alumina as a support or carrier for the platinum component without the attendant disadvantages of the prior art catalysts, since in accordance with the present invention the acid centers desired for accomplishing reforming are located on separate particles distinct from those employed as a carrier for the platinum metal component. It is accordingly a preferred embodiment of this invention to employ as the platinum metal bearing component, a carrier consisting of alumina having impregnated thereon between about 0.05 and 5 percent by weight and more particu-

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larly between about 0.1 and about 2 percent by weight of platinum.

The platinum metal may be deposited on the carrier in any suitable manner. One feasible method is to admix particles of the carrier with an aqueous solution of an acid of the metal, for example, chloroplatinic or chloropalladic acid or of the ammonium salt of the acid, of suitable concentration. The impregnated particles are then dried and treated with hydrogen at elevated temperatures to reduce the chloride to the metal and to activate the catalyst.

It is contemplated that the cracking component of the present catalyst may be produced by any of the usual methods, well known in the art, employing cogellation or impregnation techniques. Thus, taking the preparation of silica-alumina composites as a typical example, cogels of silica and alumina may be prepared by intimately admixing an acidic solution of an aluminum salt with sodium silicate to yield a silica-alumina hydrosol which sets after lapse of a suitable period of time, to a hydrogel. The resulting hydrogel is thereafter water-washed, base-exchanged to remove zeolitic sodium, dried, preferably in superheated steam and finally calcined at 900 to 1400° F. in air. Alternately, a silica-alumina composite may be produced by separately forming a hydrogel or gelatinous precipitate of silica and a hydrogel or gelatinous precipitate of alumina and ball-milling or otherwise intimately admixing the silica and alumina together to yield a resultant silica-alumina composite. In such instances the silica is suitably prepared by mixing an acid solution, for example, an aqueous sulfuric acid solution, with sodium silicate. If it is desired to prepare silica initially free of alkali metal ions, such may be accomplished by effecting hydrolysis of alkyl silicates, i. e. ethyl silicate. Alumina is readily prepared by the addition of ammonium or alkali metal hydroxide to an aqueous aluminum salt solution, for example, an aluminum salt of a mineral acid, such as aluminum nitrate, aluminum chloride or aluminum sulfate. As another alternate procedure for preparing the silica-alumina composite, a synthetic silica gel or precipitate may be prepared in accordance with one of the foregoing processes and alumina may be deposited thereon by contacting the silica gel or precipitate with an aqueous aluminum salt solution, followed by the addition of a sufficient amount of ammonium hydroxide to effect precipitation of alumina on the silica. The composite of silica and alumina can further be prepared by contacting a preformed silica gel with an aqueous aluminum salt solution, thereafter removing the impregnated silica gel from the solution and heating to a sufficiently elevated temperature to decompose the aluminum salt laid down by impregnation to alumina so that the resulting product is silica impregnated with the requisite amount of alumina. All of the foregoing methods for preparing composites of alumina and silica are well known in the art and are referred to herein merely as exemplary of suitable preparation procedures. It will be realized that composites of other oxides than silica and alumina and composites of more than two oxides may with suitable modification likewise be prepared in accordance with the general procedures above outlined.

It is also feasible to produce the cracking component in the form of spheroidal particles such as beads following the teachings of Marisc set forth in U. S. 2,384,946, or in the form of uniformly shaped pellets prepared by casting or extrusion methods. The cracking component may also be prepared as a mass which is thereafter broken up into irregularly shaped pieces. In all of the foregoing procedures, the particles or pieces of produced cracking component are ground to finely divided particles having a requisite particle diameter of less than 100 microns. It is also feasible to initially produce the cracking component in the form of finely divided particles of requisite particle size by employing

techniques used in the preparation of fluid catalyst particles, for example by spraying or rapid agitation of a hydrosol to form minute particles of hydrosol that set to particles of hydrogel which upon drying yield discrete gel particles having a diameter of less than 100 microns.

As indicated hereinabove, the preferred cracking component is a synthetic composite of silica and alumina. It was also noted above that the cracking component should in accordance with the present invention fulfill the requirement that:

$$n \times A. I. = 2 \text{ to } 30, \text{ and preferably } 10 \text{ to } 25$$

where n is the weight fraction of cracking component in the catalyst mixture and $A. I.$ is the activity index of said component. It has further been discovered that when a synthetic cogelled silica-alumina composite is employed as the cracking component, the foregoing requirement may be expressed in the form of a critical relationship between the alumina content and the surface area of the composite. Thus, it has been found that hydrocarbon fractions of low octane rating can be converted into hydrocarbon fractions of high octane rating by subjecting the same to hydroforming in the presence of a catalyst consisting essentially of a mechanical mixture of particles, less than 100 microns in diameter of an inert carrier impregnated with a specified small amount of a platinum metal and a cracking component consisting essentially of cogelled silica-alumina, the relationship between the alumina content and surface area of said cracking component being governed by the following expression:

$$n \times S. A. \times Al_2O_3 = 700 \text{ to } 950$$

where n has the above designated significance, $S. A.$ is the surface area in square meters per gram of the cracking component and Al_2O_3 denotes the weight percent alumina content in the silica-alumina cogelled cracking component. The surface area of cogelled silica-alumina cracking component employed herein generally is between about 35 and about 500 square meters per gram and the alumina content of said component is generally between about 1 and about 20 percent by weight, the overall relationship between surface area and alumina content being governed by the above expression.

It is emphasized that such expression is applicable to cogelled silica-alumina composites. In those instances where an impregnated type silica-alumina cracking component is employed, i. e. silica having alumina deposited thereon rather than cogelled therewith, it has been discovered that the relationship between alumina content and surface area is governed by the following expression:

$$n \times S. A. \times Al_2O_3 = 170 \text{ to } 250$$

where n , $S. A.$ and Al_2O_3 have the above-designated significance. The surface area of cracking components employed herein in which silica is impregnated with alumina is generally between about 35 and about 500 square meters per gram and the alumina content of such type composites is generally between about 5 and about .25 percent by weight, the overall relationship fulfilling the requirements of the above expression.

The surface area of the foregoing silica-alumina composites of either the cogelled or impregnated type can be adjusted, if necessary, by suitable well known methods. Thus, the surface area can be controlled by subjecting the composites to heat treatment at elevated temperatures in air or by subjecting the composites to steam treatment or treatment with fluorides, for example, with HF or NH_4F . A particular suitable method for adjusting the surface area is by subjecting the composite to hydrothermal treatment at a temperature between about 400 and about 900° F., for a period of between about 1 minute and about 6 hours under a pressure between about 100 and about 3000 pounds per square inch. Such method of hydro thermal treatment is described in detail in copending application

Serial Number 217,308 filed March 23, 1951, by Plank et al. and issued as U. S. 2,698,305.

A preferred catalyst, as indicated above, is one consisting essentially of a mechanical mixture of finely divided particles of alumina having platinum deposited thereon and finely divided particles of silica-alumina cracking component. This catalyst may be used in the form of a powdered mixture in a fluidized type reactor. Alternatively, the composite powder may be pelleted for use in static reactors. It has been conventional practice in obtaining hard pellets to initially mix the material undergoing pelleting with a binder, such as stearic acid and to subsequently remove such binder from the formed pellets by burning. Since the high temperatures necessarily employed to effect substantially complete removal of the binder from the pelleted product by combustion may adversely affect the platinum metal, it is preferred to prepare the platinum-containing catalyst pellets of this invention by initially admixing alumina carrier particles having a particle diameter of less than 100 microns with silica-alumina particles having a particle diameter of less than 100 microns and pelleting the resulting composite with a binder of the conventional type, i. e. one which is capable of being subsequently removed from the pelleted product by combustion. The pellets of alumina and silica-alumina so obtained are then heated in an oxygen-containing atmosphere to a temperature sufficient to burn out the binder. The pellets, after cooling, are then brought into contact with a solution containing platinum as an anion, the time of such contact being sufficient to fill the pores of the pelleted composite with impregnating solution. The impregnated pellets are thereafter removed from the solution and permitted to remain under non-drying conditions for a period of time sufficient to allow the platinum from the solution to reach an adsorption equilibrium between the alumina and silica-alumina surfaces. Such time may extend from about 15 minutes to 30 hours depending on the size of the particles. The pelleted composite is thereafter dried and the deposited platinum compound is reduced to elemental platinum by treating with hydrogen. By following the foregoing procedure substantially all of the platinum is deposited on the alumina particles of the composite and very little is deposited on the silica-alumina component of the catalyst. The above procedure takes advantage of the relatively high adsorption constant of alumina for the platinum anion and the comparatively low adsorption constant of the silica-alumina component. Thus, it is estimated that under the above outlined conditions of impregnation, less than $\frac{1}{100}$ of the platinum deposited is laid down on the silica-alumina particles. Other of the inert carriers employed herein having a high adsorption constant for the platinum anion, such as activated carbon may likewise be used in place of the alumina in the above method. It may be noted that silica, due to its relatively low adsorption constant for the platinum anion cannot be employed in the above procedure since the differential between the adsorption characteristics of silica and silica-alumina components is not sufficiently great to afford the desired selective adsorption of platinum on the inert carrier.

Reforming, in accordance with the present process, is generally carried out at a temperature between about 700° F. and 1000° F. and preferably at a temperature between about 800° F. and about 975° F. The pressure during reforming is generally within the range of about 100 to about 1000 pounds per square inch gauge and preferably between about 200 and about 700 pounds per square inch gauge. The liquid hourly space velocity employed, i. e. the liquid volume of hydrocarbon per hour per volume of catalyst is between about 0.1 and about 10 and preferably between about 0.5 and about 4. In general, the molar ratio of hydrogen to hydrocarbon charge employed is between about 1 and about 20 and preferably between about 4 and about 12.

Hydrocarbon charge stocks undergoing reforming, in

accordance with this invention, comprise mixtures of hydrocarbons and particularly petroleum distillates boiling within the approximate range of 60° F. to 450° F., which range includes naphthas, gasolines and kerosene. The gasoline fraction may be a full boiling range gasoline. It is, however, preferred to use a selected fraction, such as naphtha having an initial boiling point of between about 150° F. and about 250° F. and an end boiling point of between about 350° F. and about 425° F.

The following examples will serve to illustrate the process of the invention and to establish the criticality of the particle size of the components making up the instant catalyst.

The examples were carried out with a synthetic naphtha consisting of 50 mole percent of n-heptane and 50 mole percent of cyclohexane. A desirable reforming catalyst will, for such charge, show a high yield of isomerized heptanes along with a high yield of benzene obtained from the cyclohexane. The reaction conditions involved the use of a liquid hourly space velocity of 2, a hydrogen to hydrocarbon ratio of 4 and a total pressure of 350 p. s. i. g.

The single figure of the drawing shows the yields of benzene and isooheptane obtained with three catalysts:

Example 1 employed a catalyst consisting of a mechanical mixture of a silica-alumina cracking component and platinum deposited on a carrier of silica gel. The particle size of each of the components was in the range of 14 to 20 mesh.

Example 2 employed a catalyst consisting of a mechanical mixture of a silica-alumina cracking component and platinum deposited on a carrier of silica gel. The particle size of each of the components in this example was in the range of 100–200 mesh. In other respects, the catalyst was identical with that employed in Example 1.

Example 3 employed a standard reforming catalyst of 14–18 mesh in which platinum was deposited on a silica-alumina composite.

Data with reference to the catalyst composition for each of the above examples are tabulated below:

Example	Wt. of SiO ₂ Gel* (Grams)	Wt. of SiO ₂ —Al ₂ O ₃ ** (Grams)	Total Wt. of Catalyst (Grams)	Total Wt. of Pt in Reactor (Grams)	Total Acid Surface Area in Reactor (Square Meters)
1.....	6.7	10.9	17.6	.047	1,540
2.....	6.7	10.9	17.6	.047	1,540
3.....	—	23.6	23.6	.047	1,540

*SiO₂ gel of .41 gram/cc. density; surface area about 500 m.²/g.

**SiO₂—Al₂O₃; surface area in Examples 1 and 2 was 141 m.²/g.; in Example 3 surface area was 69 m.²/g.

In the above examples, the particles of each component were mixed and pelleted in the absence of a binder under a pressure of about 120,000 p. s. i. g. to pellets of $\frac{3}{16}$ " diameter and $\frac{3}{32}$ " length.

It will be seen from the attached figure graphically setting forth the results of reforming with each of the above catalysts that the activity characteristics of the mechanical mixture approach those of the standard catalyst (Example 3) at a particle size in the range of 100–200 mesh (Example 2). With a catalyst of appreciably greater particle size (Example 1) the desired activity was not achieved. Accordingly, it is an essential feature of this invention that the particle size of each of the components comprising the mechanical catalyst mixture described hereinabove be greater than about 100 mesh (Tyler) or less than about 100 microns in diameter.

In the foregoing examples, the total acid surface area for the reactor was adjusted by selecting the weight of the silica-alumina component in the mechanical mixture, taking into account the surface area at hand.

The ability to choose the amount of acid cracking component to be incorporated in the ultimate catalyst mix-

ture allows the use of cracking component having a wide range of surface area. One of the advantages of the mixed catalyst system of this invention resides in the ability to use a variety of available starting materials without the need of either activation or deactivation techniques to adjust acidity of the catalyst. For example, spent cracking catalysts deactivated by age having surface areas of about 150 square meters per gram could be employed directly as a cracking component of the instant catalyst. In addition, since small amounts of metals which accumulate in catalytic cracking operations have no deleterious effect in reforming reactions, it is feasible to use metal-poisoned cracking catalyst which would otherwise be discarded as useless, for the cracking component of the instant mechanical catalyst mixture.

The process of this invention accordingly affords complete and immediate flexibility in catalyst composition within the limits set forth hereinabove. Thus, in changing types of charge stocks, such as between paraffinic and naphthenic stocks, the catalyst composition can be adjusted immediately in accordance with this invention by adding or withdrawing one or the other catalyst component. For example, in transferring to more naphthenic charge stocks, more cracking component in the present mechanical catalyst mixture will serve to increase the yield of C₄⁺ gasoline. On the other hand, in transferring to paraffinic stocks a relatively greater emphasis on the platinum metal component is desirable to reduce the cracking reaction and to emphasize dehydrocyclization. In similar manner, fluctuation in the demand for excess butanes can be adjusted by the same expedient.

The fact that the platinum metal and cracking catalyst components utilized in the present mechanical catalyst mixtures have generally different properties on the one hand but are seen to be operable as physically independent or separable entities on the other hand, affords a basis for improved reforming processes, with regard to catalyst regeneration and methods for the recovery of the valuable platinum metal constituent of the catalyst after the same has become catalytically spent.

Thus, platinum-containing reforming catalysts of the type heretofore employed in which platinum is impregnated on a cracking base have been regenerated by contacting the spent catalyst with air or other oxygen-containing gas at an elevated temperature sufficient to burn carbonaceous deposits from the catalysts. Careful control of the rate of burning and temperature during regeneration of such catalysts have been necessary in order not to impair the catalytic activity of the platinum component. The usual procedure in effecting such regeneration has involved initial contact of the spent catalyst at a temperature in the range of 900 to 950° F. with a gas of low oxygen content (about 2 volume percent) and gradual increase of the oxygen concentration during the regeneration period until pure air or oxygen is being used. It is important in such procedures that the regeneration temperature be maintained below 1000° F.

By utilizing the mechanical catalyst mixture of this invention, it is possible to provide means for ready regeneration of the cracking component without subjecting the platinum metal to the severity of such regeneration. Thus, the catalyst of the present invention, after becoming spent, may be separated into its components of platinum-containing particles and cracking catalyst particles by providing such components with a suitable different physical characteristic which permits their ready separation, such as a difference in particle size. Thereafter, the cracking component may be directly recycled to the reactor, discarded, or regenerated by contacting with an oxygen-containing gas, i. e. air for a sufficient time and at a sufficiently elevated temperature to burn carbonaceous material therefrom but under conditions such that sintering of the cracking component is not encountered. Generally these conditions are fulfilled by regenerating in air for a period in the range of 10 minutes

to about 1 hour and at a temperature in the approximate range of 1000° F. to 1400° F. The separated platinum-containing component may likewise be directly recycled to the reactor, discarded or regenerated by undergoing extraction with a suitable acid solution, such as aqua regia. The resulting acid solution of platinum may then be used in impregnation of fresh particles of inert carrier, which particles are subsequently recycled to the reactor. In those instances wherein a pelleted composite of cracking component and platinum-containing component is employed, the catalyst mixture may be separated into its components by initially crushing to a particle size comparable to or below the magnitude of the small constituent particles, and thereafter separating the component particles by flotation, air-blowing, sifting or by any of the various other known means for separating physically and/or chemically different materials. The separated cracking and platinum-containing components may then be separately regenerated. The above methods applicable for regeneration of hydrocarbon conversion catalysts consisting essentially of mechanical mixtures of a cracking component and a platinum-containing component, have been described in greater detail in my copending application Serial No. 442,975, filed July 13, 1954.

It is accordingly to be understood that the above description is merely illustrative of preferred embodiments of the invention of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

What is claimed:

1. A process for reforming a hydrocarbon mixture which comprises contacting the same under reforming conditions with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 and about 5% by weight of a platinum metal and (2) an acidic cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A. I. &= 2 \text{ to } 30 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where A. I. is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with platinum metal in the mixture, C_m is the platinum metal content expressed in weight per cent of the inert carrier and d_s is the density of the inert carrier in grams per cubic centimeter.

2. A process for reforming a petroleum distillate boiling within the approximate range of 60° F. to 450° F. which comprises contacting the same at a temperature between about 700° F. and about 1000° F. at a liquid hourly space velocity between about 0.1 and about 10 in the presence of hydrogen under a pressure between about 100 and about 1000 pounds per square inch gauge and a molar ratio of hydrogen to hydrocarbon between about 1 and about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 and about 5% by weight of a platinum metal and (2) an acidic cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A. I. &= 2 \text{ to } 30 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where A. I. is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with platinum metal in the mixture, C_m is the platinum metal content expressed in weight per cent of the inert carrier and d_s is the density of the inert carrier in grams per cubic centimeter.

3. A process for reforming a hydrocarbon mixture

which comprises contacting the same under reforming conditions with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.1 and about 2% by weight of a metal selected from a group consisting of platinum and palladium and (2) an acidic cracking component consisting of silica and at least one oxide selected from the group consisting of alumina, magnesia, zirconia, and thoria, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A. I. &= 10 \text{ to } 25 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where A. I. is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with a metal selected from a group consisting of platinum and palladium, C_m is the concentration of a metal selected from a group consisting of platinum and palladium expressed in weight per cent of the inert carrier and d_s is the density of inert carrier in grams per cubic centimeter.

4. A process for reforming a petroleum distillate boiling in the approximate range of 60° F. to 450° F. which comprises contacting the same at a temperature between about 800° F. and about 975° F. at a liquid hourly space velocity between about 0.5 and about 4 in the presence of hydrogen at a pressure between about 200 and about 700 pounds per square inch gauge and a molar ratio of hydrogen to hydrocarbon between about 4 to about 12 with a catalyst consisting essentially of a mechanical mixture of particles having a size in the approximate range of 100-400 mesh and composed of (1) a porous inert carrier having deposited thereon between about 0.1 and about 2% by weight of platinum and (2) an acidic cracking component consisting essentially of silica and at least one oxide selected from the group consisting of alumina, magnesia, zirconia, and thoria, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A. I. &= 2 \text{ to } 30 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where A. I. is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with platinum metal in the mixture, C_m is the platinum metal content expressed in weight per cent of the inert carrier and d_s is the density of the inert carrier in grams per cubic centimeter.

5. A process for reforming a hydrocarbon mixture which comprises contacting the same under reforming conditions with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.1 and about 2% by weight of platinum and (2) an acidic silica-alumina cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A. I. &= 10 \text{ to } 25 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where A. I. is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with platinum metal in the mixture, C_m is the platinum metal content expressed in weight per cent of the inert carrier and d_s is the density of the inert carrier in grams per cubic centimeter.

6. A process for reforming a petroleum distillate boiling in the approximate range of 60° F. to 450° F. which comprises contacting the same at a temperature between about 700° F. and about 1000° F. at a liquid hourly space

velocity between about 0.1 and about 10 in the presence of hydrogen at a pressure between about 100 and about 1000 pounds per square inch gauge and a molar ratio of hydrogen to hydrocarbon between about 1 to about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 and about 5% by weight of a platinum metal and (2) a cogelled silica-alumina cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times S.A. \times Al_2O_3 &= 700 \text{ to } 950 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where n is the weight fraction of cogelled silica-alumina cracking component in the mixture, $S.A.$ is the surface area of the cogelled silica-alumina component in square meters per gram, Al_2O_3 is the weight per cent alumina content in the cogelled silica-alumina component, m is the weight fraction of inert carrier impregnated with a platinum metal in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier and d_s is the density of inert carrier in grams per cubic centimeter.

7. A process for reforming a petroleum distillate boiling in the approximate range of 60° F. to 450° F. which comprises contacting the same at a temperature between about 700° F. and about 1000° F. at a liquid hourly space velocity between about 0.1 and about 10 in the presence of hydrogen at a pressure between about 100 and about 1000 pounds per square inch gauge and a molar ratio of hydrogen to hydrocarbon between about 1 and about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 and about 5% by weight of a platinum metal and (2) a cracking component consisting of silica impregnated with alumina, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times S.A. \times Al_2O_3 &= 170 \text{ to } 250 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where n is the weight fraction of cracking component in the mixture, $S.A.$ is the surface area of the impregnated silica-alumina composite in square meters per gram, Al_2O_3 is the weight percent of alumina in the silica-alumina composite, m is the weight fraction of inert carrier impregnated with a platinum metal in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier and d_s is the density of inert carrier particles in grams per cubic centimeter.

8. A process for reforming a petroleum distillate boiling in the approximate range of 60 to 450° F. which comprises contacting the same at a temperature between about 800 and about 975° F. at a liquid hourly space velocity between about 0.5 and about 4 in the presence of hydrogen at a pressure between about 200 and about 700 pounds per square inch gauge and a molar ratio of hydrogen to hydrocarbon between about 4 and about 12 with a catalyst consisting essentially of a mechanical mixture made up of particles having a size in the approximate range of 100 to 400 mesh and composed of (1) a porous alumina carrier having deposited thereon between about 0.05 and about 5% by weight of platinum and (2) a cogelled silica-alumina cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times S.A. \times Al_2O_3 &= 700 \text{ to } 950 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where n is the weight fraction of cogelled silica-alumina cracking component in the mixture, $S.A.$ is the surface area of the cogelled silica-alumina component in square

meters per gram, Al_2O_3 is the weight percent alumina content in the cogelled silica-alumina component, m is the weight fraction of inert carrier impregnated with platinum in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier and d_s is the density of inert carrier in grams per cubic centimeter.

9. A process for reforming a hydrocarbon mixture which comprises contacting the same under reforming conditions with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 and about 5% by weight of a platinum metal and (2) an acidic cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A.I. &= 2 \text{ to } 30 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where $A.I.$ is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with platinum metal in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier and d_s is the density of the inert carrier in grams per cubic centimeter, separating the aforesaid mixture after reforming therewith into its components, separately regenerating each of said components, combining the regenerated components, and recycling the resulting catalyst mixture to further contact with said hydrocarbon mixture.

10. A process for reforming a hydrocarbon mixture which comprises contacting the same under reforming conditions with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.1 and about 2% by weight of a metal selected from a group consisting of platinum and palladium and (2) an acidic cracking component consisting of silica and at least one oxide selected from the group consisting of alumina, magnesia, zirconia, and thoria, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A.I. &= 10 \text{ to } 25 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where $A.I.$ is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier pregated with a metal selected from a group consisting of platinum and palladium, C_m is the concentration of a metal selected from a group consisting of platinum and palladium expressed in weight percent of the inert carrier and d_s is the density of inert carrier in grams per cubic centimeter, separating the aforesaid mixture after reforming therewith into its components, separately regenerating each of said components, combining the regenerated components and recycling the resulting catalyst mixture to further contact with said hydrocarbon mixture.

11. A method for preparing a catalyst consisting essentially of pellets made up of a mechanical mixture of particles of less than 100 microns in diameter which comprises admixing particles of less than 100 microns in diameter of alumina and particles of less than 100 microns in diameter of an acidic silica-alumina cracking component, pelleting the resulting composite under pressure with a binder, removing the binder from the pelleted product by combustion, contacting the residual pelleted composite with a solution containing platinum as an anion for a sufficient period of time to permit the pores of said residual composite to fill with said solution, permitting the impregnated particles to remain in a non-

drying atmosphere for a sufficient period of time to allow platinum from the solution to reach an adsorption equilibrium between alumina and silica-alumina surfaces, thereafter drying the composite and reducing the deposited platinum compound to elemental platinum.

12. A method for preparing a catalyst consisting essentially of pellets made up of a mechanical mixture of particles of less than 100 microns in diameter which comprises admixing particles of less than 100 microns in diameter of activated carbon and particles of less than 100 microns in diameter of an acidic silica-alumina cracking component, pelleting the resulting composite under pressure with a binder, removing the binder from the pelleted product by combustion, contacting the residual pelleted composite with a solution containing platinum as an anion for a sufficient period of time to permit the pores of said residual composite to fill with said solution, permitting the impregnated particles to remain in a non-drying atmosphere for a sufficient period of time to allow platinum from the solution to reach an adsorption equilibrium between activated carbon and silica-alumina surfaces, thereafter drying the composite and reducing the deposited platinum compound to elemental platinum.

13. A catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 and about 5% by weight of a platinum metal and (2) an acidic cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A.I. &= 2 \text{ to } 30 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where A. I. is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with a platinum metal in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier and d_s is the density of the inert carrier in grams per cubic centimeter.

14. A catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 to about 5% by weight of a platinum metal and (2) a cogelled silica-alumina cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times S.A. \times Al_2O_3 &= 700 \text{ to } 950 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where n is the weight fraction of cogelled silica-alumina cracking component in the mixture, S. A. is the surface area of the cogelled silica-alumina component in square meters per gram, Al_2O_3 is the weight percent alumina content in the cogelled silica-alumina component, m is the weight fraction of inert carrier impregnated with a platinum metal in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier and d_s is the density of inert carrier in grams per cubic centimeter.

15. A catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.05 and about 5% by weight of a platinum metal and (2) a cracking component consisting of silica impregnated with alumina, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times S.A. \times Al_2O_3 &= 170 \text{ to } 250 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where n is the weight fraction of cracking component

in the mixture, S. A. is the surface area of the impregnated silica-alumina composite in square meters per gram, Al_2O_3 is the weight percent of alumina in the impregnated silica-alumina composite, m is the weight fraction of inert carrier impregnated with a platinum metal in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier, and d_s is the density of inert carrier particles in grams per cubic centimeter.

16. A catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of (1) a porous inert carrier having deposited thereon between about 0.1 and about 2% by weight of a metal selected from a group consisting of platinum and palladium and (2) an acidic cracking component consisting of silica and at least one oxide selected from the group consisting of alumina, magnesia, zirconia, and thoria, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times A.I. &= 10 \text{ to } 25 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where A. I. is the activity index of the acid cracking component, n is the weight fraction of acid cracking component in the mixture, m is the weight fraction of inert carrier impregnated with a metal selected from a group consisting of platinum and palladium, C_m is the concentration of a metal selected from a group consisting of platinum and palladium expressed in weight percent of the inert carrier and d_s is the density of inert carrier in grams per cubic centimeter.

17. A catalyst consisting essentially of a mechanical mixture made up of particles having a size in the approximate range of 100 to 400 mesh and composed of (1) a porous alumina carrier having deposited thereon between about 0.05 and about 5% by weight of platinum and (2) a cogelled silica-alumina cracking component, the relationship between the components making up said mixture being governed by the following expressions:

$$\begin{aligned} n \times S.A. \times Al_2O_3 &= 700 \text{ to } 950 \\ m \times C_m \times d_s &= .1 \text{ to } .8 \end{aligned}$$

where n is the weight fraction of cogelled silica-alumina cracking component in the mixture, S. A. is the surface area of the cogelled silica-alumina component in square meters per gram, Al_2O_3 is the weight percent alumina content in the cogelled silica-alumina component, m is the weight fraction of inert carrier impregnated with platinum in the mixture, C_m is the platinum metal content expressed in weight percent of the inert carrier and d_s is the density of inert carrier in grams per cubic centimeter.

18. A method for preparing a catalyst consisting essentially of pellets made up of a mechanical mixture of particles of less than 100 microns in diameter, which comprises admixing particles of less than 100 microns in diameter of a porous inert carrier and particles of less than 100 microns in diameter of an acidic cracking component, pelleting the resulting composite, contacting the pelleted composite with a solution containing platinum as an anion, maintaining the impregnated pellets in a non-drying atmosphere for a sufficient period of time to allow platinum from the solution to reach an adsorption equilibrium between the surfaces of porous carrier and acidic cracking component, the latter being characterized by a distinctly lower adsorption constant for platinum anion than the former, and thereafter reducing the deposited platinum compound to elemental platinum.

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