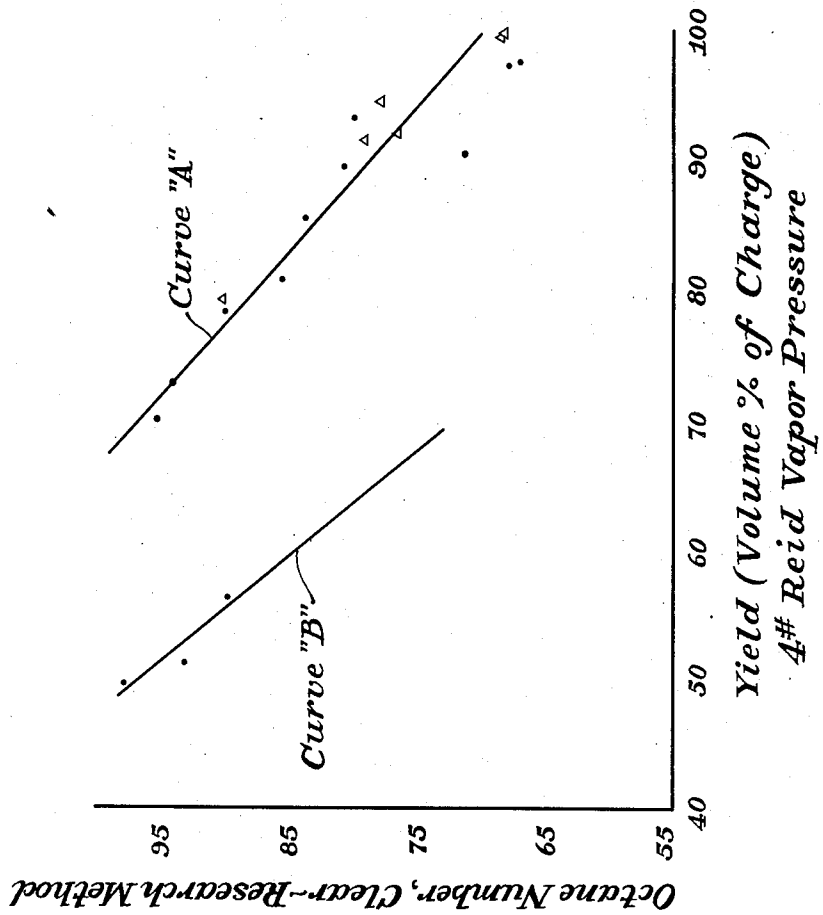
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REFORMING PROCESS AND CATALYST

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ATTEST

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REFORMING PROCESS AND CATALYST

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This invention relates generally to a process for improving low octane hydrocarbon fractions to thereby produce an increase in octane value of such fractions. More specifically, this invention is concerned with a process involving the use of a special catalyst under reforming conditions whereby low anti-knock hydrocarbon fractions can be efficiently converted to a product possessing a higher anti-knock value.

It is well known that an increase in the anti-knock properties of hydrocarbons may be accomplished by catalytic reforming under specific operating conditions. These processes generally involve the steps of passing a hydrocarbon fraction with or without added hydrogen over a reforming catalyst. Although may theories have been advanced as to the exact nature of the reactions which occur during reforming, it is generally believed that reforming involves a number of simultaneously-occurring reactions, such as isomerization, dehydrogenation, selective cracking, and aromatization. In recent years, a multitude of catalysts have been proposed for the reforming of low anti-knock gasolines. These catalysts include a majority of the elements of the periodic table in various combinations. While a number of these catalysts have been found to be effective, at least to some extent, in reforming hydrocarbon fractions, only a few of these catalytic agents are of sufficient importance to receive consideration for commercial operation since even when an effective catalyst is found, its use will not be commercially adopted unless it displays in addition to a high yield-octane relationship, the highly desirable and necessary qualities such as a long life, immunity to poisoning, and ease of regeneration. The mere fact that such a large number of reforming catalysts have been suggested in the prior art is an indication of the difficulty involved in finding a proper combination of chemical compounds which will have these desired properties.

It is an object of the present invention to provide a reforming catalyst which produces high yield-octane relationships, has a long life, is immune to poisoning, and is easily regenerated.

Another object of the present invention is to provide an improved method of reforming hydrocarbons of low octane number to hydrocarbons of high octane number.

Another object is to provide a catalyst which will have the ability to reform both high-sulfur and low-sulfur content hydrocarbon fractions.

A still further object of this invention is to provide an improved reforming catalyst containing a major proportion of a cracking component and a minor proportion of both an alkali metal and a metal from the group consisting of platinum and palladium.

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Numerous other objects will hereinafter appear from the disclosures of the specification and the appended claims, all taken in conjunction with the accompanying drawing, which portrays diagrammatically the superiority of the instant invention.

The catalysts of this invention are composite materials comprising, in general, major proportions of a cracking component hereinafter indicated, a minor proportion of a chemically combined alkali metal, and a minor proportion of platinum or palladium. More particularly, the composited material comprises the cracking component, 0.5 to 4.0 weight percent of a chemically combined alkali metal, and .01 to 2.5 weight percent of platinum or palladium. All weight percentages mentioned in this specification are based on the weight of the final composite.

The term "cracking components," as hereinafter used, shall mean a material comprising silica and at least one metal oxide from the group consisting of alumina, magnesia, thoria, and zirconia, the composite of silica with the named oxides having substantial activity for cracking hydrocarbons.

The cracking component may be derived from either naturally-occurring or synthetically produced materials. Naturally-occurring materials include various aluminum silicates, particularly when acid treated to increase their activity for cracking hydrocarbons, such as "Super Filtrol," etc. Synthetically produced cracking components include silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, silica-alumina-thoria, etc. These synthetic materials may be made in any suitable manner well known to the art, including separate, successive, or coprecipitation methods of manufacture. The preferred synthetic cracking component, silica-alumina, may be manufactured by commingling an acid, such as hydrochloric acid, sulfuric acid, etc., with commercial water glass under conditions to precipitate silica, washing with acidulated water or otherwise to remove sodium ions, commingling with an aluminum salt such as aluminum chloride, aluminum sulfate, aluminum nitrate, and either adding a basic precipitant, such as ammonium hydroxide to precipitate alumina, or forming the desired oxide or oxides by thermal decomposition of the salt as the case may permit.

The preferred cracking component, silica-alumina, may contain from 20% to 95% by weight of silica with the remainder alumina, although amounts above and below this range may also be used. A commercially available synthetic silica-alumina cracking catalyst is sold under the name "Diakel" and comprises about 87% silica and 13% alumina, prepared in general according to the method outlined above. The cracking component may be in the form of beads or granules either of regular or irregular size and shape. The granules may be ground or formed into pellets of uniform size and shape by pilling, extrusion, or other suitable methods.

The term "chemically combined alkali metal," as used herein and in the appended claims, refers to an alkali metal which is in true chemical combination with some other element of the catalyst and hence, does not include alkali metals in the metallic or free state, since it is clear that under the elevated temperatures employed in reforming hydrocarbons, uncombined alkali metals would vaporize or combine with hydrocarbons within the reaction chamber.

The alkali metal may be either sodium, potassium, lithium, cesium, or rubidium and may be composited and combined with the cracking component mentioned above in any suitable manner. Several illustrations are given below, but it must be understood that the recitation of these methods does not limit the invention to catalysts prepared according to these methods. The preferred method is to incorporate the alkali metal on the cracking component by a simple base exchange procedure which comprises the steps of soaking the cracking component pellets in a solution of a soluble alkali metal salt, draining off the excess alkali metal salt, washing the treated material with water, and drying. The alkali metal salt solution may be in the form of inorganic salts such as the carbonate, nitrate, sulfate, chloride, hydroxide, phosphate, dicarbonate, borate, aluminate, and the like, or salts of organic acids such as the acetate, propionate, and the like. The concentration of the alkali metal salt solution used in each particular instance will depend upon the solubility of the particular compound at the temperature of treating and upon the desired concentration of the alkali metal in the composite catalysts.

Although the preferred method of incorporating the alkali metal is by base exchange means as outlined above, the desired alkali metal content may also be incorporated by other procedures. One such method involves the incorporation of the desired amount of alkali metal during the preparation of the cracking component. For instance, as described above, synthetic silica-alumina cracking catalysts are often prepared by dispersing a silica gel in a solution of an aluminum salt after which a basic precipitant, such as ammonium hydroxide is added to precipitate alumina on the silica gel. If an alkali metal hydroxide is employed as the basic precipitant instead of ammonium hydroxide, the resulting compound comprises an alkali metal aluminum silicate. This compound can then be washed with a calculated quantity of a mineral acid to remove only a part of the alkali metal so that the desired critical amount of alkali metal will remain combined with the silica-alumina. Alternatively, the aluminum salt may be partially precipitated with an alkali metal hydroxide (to incorporate the necessary amount of alkali metal) following which the precipitation of the aluminum salt is completed with ammonium hydroxide and the composite calcined to remove ammonia.

It is also possible to obtain the desired amount of alkali metal by total absorption on the cracking components of a measured quantity of an alkali metal salt having a volatilizable or decomposable anion followed by drying and calcining.

The platinum or palladium may be composited with the cracking component and chemically combined alkali metal by any suitable method known to the art. The preferred method is to admix an aqueous solution of chloroplatinic acid or chloropalladic acid of suitable concentration with the cracking component containing the alkali metal. The mixture is then dried and treated with hydrogen at elevated temperatures to reduce the chloride to the metal and to activate the catalyst. Although it has been found preferable to add the alkali metal salt solution to the carrier prior to impregnation with platinum or palladium, such addition might instead be made after the impregnation with platinum or palladium.

The preparation of the composite catalyst by a simple base exchange procedure will be illustrated in the following examples. It should be understood, however, that the examples are given for the purpose of illustration and the invention in its broader aspects is not limited thereto.

EXAMPLE I

250 grams of fresh silica-alumina cracking catalyst (87% silica–13% alumina) pellets was soaked in an excess of demineralized water for 30 minutes, and thereafter centrifuged to give 410 grams of a wet catalyst. To this wet catalyst was added 220 cc. of 1.44 N sodium carbonate solution and the mixture was allowed to soak for 30 minutes. The solid material was then drained to remove the excess salt solution and washed continuously with 2000 cc. of demineralized water. When tests of the wash water indicated that no sodium ions were present, the treated cracking component was dried at 212° F. for 16 to 18 hours.

200 grams of this dried material was treated with 146 cc. of a .0174 molar chloroplatinic acid solution. After this solution became absorbed on the surface of the treated cracking component, the material was dried in an oven for 16 hours at 212° F. for 2 hours at 450° F. in the presence of nitrogen, and then reduced at 450° F. for 6 hours in an atmosphere of hydrogen. Upon analysis, this catalyst was found to contain 1.3 weight percent of sodium and .27 weight percent of platinum.

EXAMPLE II

250 grams of the fresh silica-alumina cracking catalyst pellets from the same source as Example I, was soaked in an excess of demineralized water for 30 minutes and then centrifuged to give 410 grams of wet catalyst. To this wet material was then added 210 cc. of 1.01 N potassium carbonate solution and the mixture allowed to soak for 30 minutes, after which time the supernatant salt solution was drained off and the solid material was washed continuously with 2500 cc. of demineralized water. When a test of the wash water showed that potassium ions were no longer present, the treated silica-alumina was dried at 212° F. for 16 to 18 hours.

180 grams of this dried material was treated with 132 cc. of .0172 molar chloroplatinic acid solution. After the solution had been absorbed

on the solid surface, the catalyst was dried at 212° F. for 16 hours, for 2 hours at 450° F. in an atmosphere of nitrogen, and finally reduced at 450° F. for 6 hours in the presence of hydrogen. An analysis of this catalyst showed that it contained 2.4 weight percent potassium and .22 weight percent of platinum.

EXAMPLE III

350 cc. of a 2 N Na_2CO_3 solution (93 grams $Na_2CO_3.H_2O$) in 750 cc. of H_2O was poured over 250 grams of fresh silica-alumina cracking catalyst and the mixture allowed to stand for ½ hour. The supernatant liquid was poured off and another 350 cc. portion of 2 N Na_2CO_3 solution added. After standing for 30 minutes, the excess liquid was drained off and the solids washed 10 times with 350 cc. batches of water. The solids were dried overnight in an oven at 230° F. and calcined at 900° F. for 1 hour. The resulting composite, after treatment with chloroplatinic acid as outlined in Examples I and II, was found to contain .16 weight percent platinum and 2.3 weight percent of sodium.

The above examples illustrate how the instant catalyst may be prepared by single or multiple batch type procedures. However, the catalyst can be equally well prepared by a continuous percolation of the alkali metal salt solution over the silica-alumina until the desired amount of alkali metal has been incorporated therewith.

Composite catalysts containing cesium, lithium, and rubidium may be prepared in a similar manner.

The present invention entails the use of the catalyst described above in a reforming process. The general procedure in reforming involves mixing the hydrocarbon fraction to be treated with hydrogen and passing the admixture in contact with the reforming catalyst. In carrying out reforming in accordance with this invention, temperatures in the range of 600° F. to 1000° F. and preferably 700° F. to 1000° F. may be used, depending upon the particular hydrocarbon feed employed and the particular catalyst composition ratio being used. It has been found preferable to preheat both the charge and the catalyst to these temperatures to achieve best results, although either the charge or the catalyst alone could be so heated. The process is conducted at pressures from 100 to 1000 p. s. i. and preferably from 500 to 800 p. s. i. Hourly liquid space velocities (meaning the liquid volume of hydrocarbon per hour per volume of catalyst) may be in the range of 0.1 to 10, preferably in the range of 0.5 to 4.0. The reaction may be carried out in the presence of hydrogen in amounts from 1 to 20 mols of hydrogen per mol of hydrocarbon. Under these circumstances, using the instant novel catalyst, it is possible to obtain from petroleum distillate fractions, particularly gasoline fractions, excellent yields of high octane gasoline.

The hydrocarbons to be treated in the invention comprise petroleum distillate fractions, including naphthas, gasoline, and kerosene, and particularly gasoline fractions. The gasoline fraction may be a full boiling range gasoline having an initial boiling point within the range of about 50° F. to about 90° F. and a final boiling point within the range of about 375° F. to about 425° F., or it may be a selected fraction thereof which usually will be a higher boiling fraction, commonly referred to as naphtha, and generally having an initial boiling point of from 150° F. to about 250° F. and a final boiling point within the range of about 350° F. to about 425° F. The kerosene boiling range is generally between 350° F. and 525° F.

The process of the invention may be effected in any suitable equipment and an especially suitable process comprises the fixed bed process in which the catalyst is used in the form of pellets or granules in a reaction zone or zones, the hydrocarbon and hydrogen passing through such zone or zones and in contact with the catalyst. Another suitable apparatus in which the process may be conducted is the fluid bed type in which the catalyst is suspended by the gaseous hydrocarbon stream or the moving bed type process in which the catalyst and hydrocarbon are passed either concurrently or countercurrently to each other. After reforming, the products may be fractionated to separate excess hydrogen and to recover the desired fractions of reformed product.

In one manner of operation of the process, sufficient hydrogen will be produced in the reforming reaction to maintain a hydrogen partial pressure sufficient to saturate the hydrocarbon fragments formed therein. However, hydrogen from an extraneous source is added at the beginning of the operation and usually it is desirable to recycle hydrogen within the process after the starting operation in order to assure a sufficient hydrogen atmosphere in the reaction zone. Hydrogen serves to maintain the catalyst activity by reducing or preventing carbon deposition. Also, if desired, the hydrocarbon may be treated to remove sulfur prior to reforming, athough such removal is not necessary, and in fact, the use of the instant reforming catalyst produces equally good results with or without sulfur removal.

After a period of service, it may be desirable to reactivate the catalyst, and this may be readily accomplished by passing air or other oxygen-containing gases therethrough in order to burn carbonaceous deposits from the catalyst. A particularly suitable method of regeneration comprises effecting the regeneration at a temperature of about 900° F. to 950° F., starting with a gas containing about 2% oxygen or less and gradually increasing the oxygen concentration so that at the end of the regeneration period, pure air is being passed over the catalyst. However, it is important that the temperature of regeneration should not exceed 1000° F., as it has been found that temperatures in excess of 1000° F. tend to impair the reforming activity of the catalyst.

Table 1 below comprises a series of reforming runs whereby a vaporized East Texas charge stock having the following specifications:

Reid vapor pressure	1.0
Percent sulfur	.008
Octane number, clear (Research Method, A. S. T. M. D-908-49T)	54.0
A. S. T. M. Distillation:	
Overpoint °F.	185
50% °F.	262
90% °F.	334
Endpoint °F.	367
A. P. I. Gravity at 60° F	55.5

was mixed with hydrogen (10 mols of hydrogen per mol of hydrocarbon) at a pressure of 500 p. s. i., a liquid space velocity of 1.0 (cc. of liquid per cc. of catalyst per hour) and contacted with a silica-alumina-platinum-alkali metal catalyst having the weight percent of alkali metal and platinum indicated, at the tempertures shown. These catalysts were prepared according to the

methods set forth in Examples I and II. The volume percent recovery and clear research method octane results were tabulated on the basis of a 4 pound Reid vapor pressure and plotted as curve "A" in Figure 1.

Table 1

Alkali Metal	Sodium		Sodium		Sodium		Potassium		Potassium		Cesium
Alkali Metal (Wt. %)	2.9		2.3		1.3		2.4		1.4		3.6
Platinum (Wt. Percent)	.12		.25		.27		.22		.18		.24
Temperature (° F.)	850	920	850	920	850	920	850	920	850	920	920
Yield (Vol. Percent of charge)	99.8	93.2	97.3	90.4	85.5	72.8	97.5	89.5	81.3	70.0	78.4
Research Octane (Clear)	69.9	80.0	68.0	76.4	83.8	94.2	66.9	80.7	85.6	95.2	90.0

As hereinbefore set forth, a multitude of reforming catalysts have been suggested in the prior art. Among these, the combination of platinum or palladium with a cracking component comprising silica and one or more metal oxides from the group consisting of alumina, magnesia, thoria, and zirconia have been mentioned, and particularly the combination of silica, alumina, and platinum. In order to clearly show the marked superiority of the instant catalysts over a silica-alumina-platinum catalyst not containing an alkali metal, many comparative tests were conducted.

The only method of comparing the reforming ability of two reforming catalysts is by comparing the yield-octane relationship obtainable from each. In order to make these relationships truly comparable, it is necessary to reform aliquot portions of the identical charge stock with each catalyst. If the same charge stock is not used in each case, no valid comparison of yield-octane results can be made since each different charge stock is composed of different components and consequently, each different charge stock varies in its ability to be reformed. Also, in order to make a valid comparison of the yield-octane results, it is necessary that the products be condensed at the same temperature and compared at the same Reid vapor pressure.

Therefore, to produce a silica-alumina-platinum catalyst for purposes of comparison, the steps of Examples I and II were carried out with the exception that the alkali metal treating step was omitted. This catalyst was then used to reform the identical East Texas hydrocarbon charge stock employed in the runs of Table 1 and under the same operating conditions. The results are tabulated in Table 2 below and plotted in curve "B" of Figure 1.

Table 2

Alkali Metal	None	None	
Platinuu (wt. percent)	.25	.25	
Temperature (°F.)	920	850	920
Yield (Volume percent of Charge)	51.74	56.2	49.6
Research Octane (Clear)	93.2	89.8	97.8

A comparison of Tables 1 and 2 and the corresponding curves "A" and "B" of Figure 1 shows the striking superiority of the silica-alumina platinum-alkali metal catalyst over a silica-alumina-platinum catalyst containing no alkali metal. Figure 1, attached hereto, is presented primarily to show the comparative values of the above-mentioned catalyst and is not intended to limit applicant's invention to this particular hydrocarbon feed nor is it limited to the yield-octane results obtained. The relationship of yield-octane results shown in Figure 1 for the two catalysts as been found to hold true for all feed stocks tested. Other charge stocks used with the instant catalysts may give higher yields and higher octane values, yet the relative improvement evidenced by the instant catalyst will generally the same.

It has heretofore been mentioned that the amounts of alkali metal which can be composited with the cracking component and platinum lies between optimum limits. If amounts less than 0.5% are used, the final catalyst will show yield-octane relationships falling in the neighborhood of the curve "B" in Figure 1, i. e., these catalysts are similar to silica-alumina-platinum having no alkali metal composited therewith and therefore are inferior. The upper limit of 4.0% was selected for the reason that catalysts having amounts of alkali metal in excess of this amount were too inactive, that is, they gave negligible octane improvement. However, in the case of cesium and rubidium, which have higher atomic weights, amounts somewhat in excess of 4.0% may be used without obtaining an inactive catalyst.

It has also been mentioned that the amounts of platinum or palladium should range between 0.01% by weight to 2.5% by weight of the final composite. Amounts less than 0.01% result in too low reforming activity, i. e., negligible octane improvements, amounts greater than 2.5% are likewise undesirable for the reason that such catalysts result in excessive cracking.

A further highly advantageous property of the silica-alumina-platinum-alkali metal catalyst resides in its ability to reform hydrocarbon charge stocks containing large amounts of sulfur compounds. As is well-known in the art, charge stocks containing even small amounts of sulfur compounds are much more difficult to reform than sulfur-free charge stocks. In addition, the vast majority of reforming catalysts known heretofore are deleteriously affected by a sulfur-containing feed with the result that the activity and life of these catalysts are impaired to a great degree. As a consequence, in early every reforming process known heretofore, it has been specifically pointed out that the hydrocarbon charge should be desulfurized so as to make it practically sulfur-free. Various desulfurization processes are known, but their use entails additional equipment and considerable expense. The instant catalysts, however, are not deleteriously affected by sulfur-containing charge stocks, but to the contrary are capable of reforming sulfur-containing charge stocks with the same degree of success as sulfur-free charge stocks. This highly advantageous property results in increased economy of operation by eliminating the necessity for an expensive pre-desulfurization step.

The results tabulated in Table 3 below illustrate that the present catalysts are highly efficient for reforming a hydrocarbon charge stock containing sulfur compounds. The data shown in Table 3 was obtained by passing a West Texas Permian charge stock having the following properties:

Reid vapor pressure (lbs.)	.5
Percent sulfur	.32
Octane number, clear (Research Method, A. S. T. M. D-908-49T)	48.9
A. S. T. M. distillation:	
Overpoint °F	193
50% °F	275
90% °F	334
Endpoint °F	384
A. P. I. gravity (at 60° F.)	53.2

in admixture with hydrogen (10 mols of hydrogen per mol of hydrocarbon) at a pressure of 500 p. s. i., a liquid space velocity of 1.0 (cc. of liquid per cc. of catalyst per hour) over a silica-alumina-platinum-alkali metal catalyst having the weight percent of alkali metal and platinum indicated, and at the temperatures shown in Table 3 below. These catalysts were prepared according to the methods set forth in Examples I, II, and III. The volume percent recovery and research method octane results were tabulated on the basis of a 4 pound Reid vapor pressure product.

Table 3

Alkali Metal	Sodium		Sodium		Sodium	
Alkali Metal (Wt. percent)	2.3		2.9		1.35	
Platinum (Wt., percent)	.16		.25		.25	
Temperature (°F.)	850	920	850	920	850	920
Yield (Vol. percent of Charge)	99.4	91.3	99.7	94.7	92.0	79.2
Research Octane (Clear)	68.5	79.1	68.1	78.0	76.7	90.2

The yield-octane results shown in Table 3 were plotted in Figure 1 as triangular points and it is seen that these points fall on the same yield-octane curve "A" which was obtained by reforming the low sulfur content East Texas charge stock employed in Table 1. It is evident, therefore, that a silica-alumina-platinum-alkali metal catalyst is capable of producing high yields of liquid products having high octane values when reforming even high sulfur-content hydrocarbons which have heretofore been considered difficult to reform.

I claim:

1. A process for reforming a gasoline fraction to increase the anti-knock value thereof which comprises admixing hydrogen with said fraction and passing said admixture at reforming conditions including a temperature within the range of 600° F. to 1000° F. and a pressure of from 100 to 1000 p. s. i. over a catalyst consisting essentially of a cracking component, 0.01 to 2.5 weight percent of a metal from the group consisting of platinum and palladium, and 0.5 to 4.0 weight percent of a chemically combined alkali metal, said cracking component comprising silica and at least one metal oxide from the group consisting of alumina, magnesia, thoria, and zirconia.

2. The process according to claim 1 wherein the catalyst consists essentially of 0.01 to 2.5 weight percent of platinum, 0.5 to 4.0 weight percent of chemically combined alkali metal and a cracking component comprising silica and alumina.

3. The process according to claim 1 wherein the catalyst consists essentially of 0.01 to 2.5 weight percent of platinum, 0.5 to 4.0 weight percent of chemically combined sodium, and a cracking component comprising silica and alumina.

4. A catalyst consisting essentially of a cracking component, 0.01 to 2.5 weight percent of a metal from the group consisting of platinum and palladium, and 0.5 to 4.0 weight percent of a chemically combined alkali metal, said cracking component comprising silica and at least one metal oxide from the group consisting of alumina, magnesia, thoria, and zirconia.

5. A catalyst consisting essentially of 0.01 to 2.5 weight percent of platinum and 0.5 to 4.0 weight percent of a chemically combined alkali metal, and a cracking component comprising silica and at least one metal oxide from the group consisting of alumina, magnesia, thoria, and zirconia.

6. A catalyst consisting essentially of 0.01 to 2.5 weight percent of platinum, 0.5 to 4.0 weight percent of chemically combined sodium, and a cracking component comprising silica and alumina.

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