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REFORMING PROCESS AND CATALYST THEREFOR

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This invention relates to a reforming process and to the manufacture of catalysts for use therein.

The term "reforming" is well known in the petroleum industry and refers to the treatment of gasoline fractions to improve the anti-knock characteristics thereof. The gasoline fraction may be a full boiling range gasoline having an initial boiling point within the range of from about 50° to about 100° F. and an end boiling point within the range of from about 350° 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 will have an initial boiling point of from about 150° to about 250° F. and an end boiling point within the range of from about 350° to about 425° F.

The present invention is particularly applicable to the reforming of straight run gasolines which contain naphthenic hydrocarbons, particularly cyclohexane compounds, and paraffinic hydrocarbons which usually are of straight chain or slightly branched chain structure, as well as varying proportions of aromatic hydrocarbons. In order to obtain best results in reforming operations, it is desired to dehydrogenate the naphthenic hydrocarbons to produce aromatics, to cyclisize the straight chain paraffinic hydrocarbons to form aromatics, as well as to effect a controlled type of cracking which is selective both in quality and quantity. In addition, various other concomitant reactions occur such as isomerization, hydrogen transfer, etc.

The cracking or splitting of carbon to carbon bonds is one of the important factors in a successful reforming process. Controlled or selective cracking is highly desirable since such cracking will result in a product of improved anti-knock characteristics. In general, the lower molecular weight products have higher octane numbers, and thus a final gasoline product of lower average molecular weight will usually have a higher octane rating. Furthermore, during the cracking reaction, isomerization or other molecular rearrangement occurs which also results in products having higher anti-knock characteristics. The selective cracking is also of particular advantage when the charging stock contains components boiling above about 400° F. in order to convert these components to fractions boiling below about 400° F. It is thus seen that the selective cracking results not only in an improved quality product but also in an increase in quantity of the desired products.

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However, the cracking must be selective and must not result in the decomposition of the normally liquid hydrocarbons substantially or completely into normally gaseous hydrocarbons. The desired selective cracking generally comprises the splitting of a higher boiling hydrocarbon molecule into two molecules both of which are normally liquid hydrocarbons. To a lesser extent it comprises the removal of methyl, ethyl and, to a still lesser extent, propyl groups, in the form of methane, ethane and propane. However, the removal of these radicals is controlled so that not more than one or possibly two of such radicals are removed from a given molecule. For example, decane may be reduced to two pentane molecules, heptane to hexane, nonane to octane or heptane, etc. On the other hand, uncontrolled or non-selective cracking will result in the decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons as, for example, by the continued demethylation of normal heptane to produce 7 molecules of methane.

Another important objection to non-selective or uncontrolled cracking is that this type of cracking will result in the more rapid formation of larger quantities of coke or carbonaceous material which deposits on the catalyst and decreases or destroys its activity to catalyze the desired reactions. This in turn results in shorter processing cycles or periods, with the necessity of more frequent regeneration of the catalyst by burning the carbonaceous products therefrom or, should the catalyst activity be destroyed, it will be necessary to shut down the unit to remove the old catalyst and replace it with new catalyst.

Another important feature in successful reforming processes is the matter of hydrogen production and consumption. Investigation has shown that the presence of hydrogen in the reforming zone further tends to decrease the amount of carbonaceous deposit on the catalyst. Reforming processes effected in the presence of hydrogen are known as "hydroforming." In view of the fact that the cost of hydrogen is quite high, it is essential that there be no net consumption of hydrogen or, in other words, at least as much hydrogen must be produced in the process as is consumed therein.

In one embodiment the present invention relates to a process for reforming a gasoline fraction which comprises subjecting said fraction to contact at reforming conditions with a catalyst prepared by combining a halogen with alumina in an amount of from about 0.1 to about

8% by weight of said alumina on a dry basis, commingling therewith a platinum compound-ammonium hydroxide solution in an amount to form a final catalyst containing from about 0.01% to about 1% by weight of platinum.

In a specific embodiment the present invention relates to a process for reforming a straight run gasoline fraction which comprises subjecting said gasoline fraction to contact at a temperature of from about 600° to about 1000° F., a pressure of from about 50 to about 1000 pounds per square inch and a weight hourly space velocity of from about 0.5 to about 10 in the presence of a catalyst as herein set forth.

In another specific embodiment the present invention relates to a method of manufacturing a catalyst which comprises combining a halogen with alumina in an amount of from about 0.1 to about 8% by weight of said alumina on a dry basis, commingling therewith a platinum compound-ammonium hydroxide solution in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum, and heating the composite in air at a temperature of from about 500° to about 1000° F.

The use of platinum as a catalyst for conversion processes has been of limited commercial acceptance because of the high cost of the catalyst. The present invention is based on the discovery that exceptionally good catalysts may be prepared to contain very low concentrations of platinum. While these catalysts may contain larger concentrations of platinum, which may range up to about 10% by weight or more of the alumina, it has been found that exceptionally good catalysts may be prepared to contain as low as from about 0.01% to about 1% by weight of platinum. Catalysts of these low platinum concentrations are particularly preferred in the present invention because of the considerably lower cost of the catalyst. It is well known that platinum is very expensive and any satisfactory method of reducing the amount of platinum considerably reduces the cost of the catalyst and thus enhances the attractiveness of the catalyst for use in commercial processes.

However, in order to obtain improved results with these low platinum concentrations, it is necessary that a particular type of supporting component must be composited with the platinum. It has been found that alumina shows unexpected advantages for use as a supporting component for the low platinum concentrations, apparently due to some peculiar association of the alumina with the platinum, either as a chemical combination or as a physical association. It has been found that the specific combination of alumina and low platinum concentration, not only to be a very active catalyst, but also to have a long catalyst life; that is, the catalyst retains its high activity for long periods of service. After these long periods of service, the catalyst may show a drop in activity and it has further been found that the particular combination of alumina and platinum renders the catalyst susceptible to ready regeneration.

As another essential feature of the present invention, impregnation of the alumina must be effected in the presence of ammonium hydroxide. A particularly suitable method of impregnation is by means of a solution of a suitable platinum compound. However, it has been found that, unless the impregnation is effected in the presence of ammonium hydroxide solution, uneven distribution of the platinum in or on the alumina particles is obtained. Usually this uneven distribution comprises surface coating, that is the platinum compound is distributed only on the surface of the particles and not evenly throughout the mass. By effecting the impregnation in the presence of ammonium hydroxide solution, even distribution of the platinum throughout the alumina particles is obtained.

A particularly satisfactory method of impregnating the alumina comprises the use of an aqueous solution of chloroplatinic acid. In a preferred embodiment, the aqueous solution of chloroplatinic acid is commingled with an ammonium hydroxide solution and the mixture is added to alumina particles. In another embodiment, the ammonium hydroxide solution may be added to the alumina particles and the chloroplatinic acid solution is thereafter added to the mixture. In still another embodiment, the chloroplatinic acid solution may be added to the alumina particles and the ammonium hydroxide solution is thereafter added. In any event, the mixture is allowed to stand, preferably with or after suitable agitation, so that thorough mixing is obtained and even distribution of the platinum throughout the alumina particles is effected.

In its preferred embodiment, the present invention is directed to the use of ammonium hydroxide solution in order to avoid the formation, upon commingling with chloroplatinic acid, of ammonium chloroplatinate because ammonium chloroplatinate is insoluble in aqueous solutions and will not result in even distribution throughout the alumina particles. Thus, an ammonium salt as, for example, ammonium chloride, cannot be used in place of ammonium hydroxide because upon commingling of ammonium chloride with chloroplatinic acid a precipitate of ammonium chloroplatinate is obtained. Even upon heating or upon the addition of ammonium hydroxide, the precipitate will not be redissolved to form a clear solution. However, in some cases, both the addition of ammonium hydroxide and heating will redissolve the precipitate to form a clear solution and, in such cases, the use of ammonium chloride may be employed in conjunction with both ammonium hydroxide and heating.

With proper selection of the chloroplatinic acid solution and of ammonium hydroxide solution, commingling of these solutions will not form a precipitate and, therefore, will not form ammonium chloroplatinate. Applicant is not certain as to the exact chemical formula of the compound formed but it is believed to be $[Pt(NH_3)_2Cl_2]Cl_2$. In any event it is apparent that the clear solution formed upon the mixing of ammonium hydroxide with chloroplatinic acid solution is different than the ammonium chloroplatinate precipitate formed upon the addition of ammonium chloride to chloroplatinic acid solution. If ammonium chloroplatinate solution is formed, as hereinbefore set forth, or due to the use of a too highly concentrated solution of chloroplatinic acid, the ammonium chloroplatinate solution may be redissolved to form the clear solution which is no longer ammonium chloroplatinate and apparently is the compound hereinbefore set forth. The difference between the two compounds is further evidenced by the fact that the addition of carbonate ions as, by the addition of sodium carbonate, will not form a precipitate in the case of the mixture of ammonium chloride with chloroplatinic acid upon heating, but will form a precipitate in the case

of the solution of ammonium hydroxide with chloroplatinic acid upon heating.

To further improve these catalysts, it is an essential feature of the present invention that the final catalyst contains halogen ions in a specific concentration. It has been found, and will be shown in the following examples, that the presence of halogen ions within a specific range effects a considerable improvement in the catalyst. It is believed that the halogen enters into some chemical combination or loose complex with the alumina and/or platinum, and thereby serves to improve the final catalyst.

While any of the halogen ions will serve to effect improved results, fluoride ions are particularly preferred. Next in order are the chloride ions, while the bromide and iodide ions are generally less preferred. It is understood that, while all of these halogens will serve to effect an improvement, they are not necessarily equivalent.

In still another essential feature of the present invention the final composite of alumina platinum compound and combined halogen is calcined in the presence of an oxygen-containing gas, particularly air, at a temperature of from about 500° to about 1000° F. for a period of 2 to 12 hours or more. As will be shown in the following examples, calcination in the presence of air results in a final gasoline product of higher octane number than is obtained when the catalyst only is calcined in the presence of a reducing atmosphere. In still another embodiment of the invention, the final composite may be reduced in the presence of hydrogen and then calcined in the presence of air, both the reduction and calcination being effected at temperatures within the range of from about 500° to about 1000° F.

In a preferred embodiment of the invention, the alumina is formed into particles of uniform size and shape prior to impregnation with the platinum compound. As another particular feature of this embodiment, the alumina particles of uniform size and shape are subjected to calcination at a temperature above 1000° F. and preferably within the range of from about 1000° to about 1400° F. for a period of 1 to 8 hours or more. The temperature and time of heating are correlated; that is, shorter times are employed with higher temperatures and longer times are employed with lower temperatures. On the other hand, the final composite containing platinum compound must not be heated at a temperature above 1000° F. and preferably is calcined in air at a temperature of from about 500° to about 1000° F. for a period of 2 to 12 hours or more as hereinbefore set forth.

The catalyst of the present invention may be prepared in any suitable manner. A particularly preferred method is to prepare alumina by adding a suitable reagent, such as ammonium hydroxide, ammonium carbonate, etc. to a salt of aluminum such as aluminum chloride, aluminum nitrate, aluminum acetate, etc. in an amount to form aluminum hydroxide which, upon drying is converted to alumina and, in the interest of simplicity, the aluminum hydroxide is referred to as alumina in the present specification and claims in order that the percentages are based on the alumina free of combined water. It has been found that aluminum chloride is generally preferred as the aluminum salt, not only for convenience in subsequent washing and filtering procedures, but also because it appears to give best results.

After the alumina has been formed, it is generally washed to remove soluble impurities. Usual washing procedures comprise washing with water, either in combination with filtration or as separate steps. It has been found that filtration of the alumina is improved when the wash water includes a small amount of ammonium hydroxide. The severity of washing will depend upon the particular method employed in preparing the catalyst. In one embodiment of the invention, the alumina is thoroughly washed with a suitable amount of water and preferably water containing ammonium hydroxide to reduce the chlorine content of the alumina to below about 0.1%. In another embodiment of the invention this washing may be selective to retain chloride ions in an amount of from about 0.2% to about 8% by weight of the alumina on a dry basis. In accordance with this method of preparing the catalyst, the chloride ions are obtained from the original aluminum chloride and are retained in the alumina, thus avoiding the necessity of adding the halogen ions in a later step of catalyst preparation. However, it generally is difficult to control the washing procedure to retain the desired amount of halogen ion and, for this reason, it usually is preferred to wash the alumina to remove substantially all of the chlorine ions and thereafter add the halogen ions in a controlled amount. The addition of the halogen ions in this manner permits better control of the amount of halogen being added. In another embodiment of the invention, the washing may be selective to retain the chloride ions in an amount constituting a portion of the total halogen desired, and the remaining portion of the halogen is then added in a subsequent step. In this method, the halogen ion may comprise the same halogen or a mixture of two different halogens, as for example, chlorine and fluorine.

Alumina prepared in the above manner, after washing and filtration, is generally recovered as a wet cake. In a preferred embodiment of the present invention, the halogen is added at this stage of the catalyst preparation, the composite is dried to reduce the same to a moisture content of about 30%, which generally requires drying at a temperature of from about 200° to about 500° F. for a period of about 2 to 24 hours or more, and the composite is formed into particles of uniform size and shape as by pilling, extrusion or other suitable methods. In another embodiment, the alumina may be formed into particles of uniform size and shape and the halogen thereafter added. In still another embodiment the halogen and platinum addition may be effected prior to forming the composite into particles of uniform size and shape.

Regardless of the stage of catalyst preparation at which the halogen is added, the halogen may be incorporated therein in any suitable manner. However, the halogen must be added in a form which will readily react with the alumina in order to obtain the desired results and also must not leave undesired deposits in the catalyst. A preferred method of adding the halogen is in the form of an acid, such as hydrogen fluoride, hydrogen chloride, hydrogen bromide and/or hydrogen iodide. Hydrogen fluoride is preferably added as an aqueous solution for ease in handling and for control of the specific amount to be added. Another satisfactory source to be used for adding the halogen is the volatile salts, such as ammonium fluoride, ammonium chloride, etc. The ammonium ions will be removed during the subsequent heating of the

catalyst and, therefore, will not leave undesirable deposits in the catalyst. In still another method, the halogen may be added as fluorine, chlorine, bromine or iodine but, in view of the fact that the halogens are normally more difficult to handle, it is generally preferable to utilize them in the form of a solution for ease in handling. In some cases, the inclusion of certain components will not be harmful but may be beneficial, and in these cases the halogen may be added in the form of suitable salts.

The concentration of halogen ion in the finished catalyst will be within the range of from about 0.1% to about 8% by weight of the alumina on a dry basis. The fluoride ion appears to be more active and therefore will be used within the range of from about 0.1% to about 3% by weight of the alumina on a dry basis. The chloride ion will be used within the range of from about 0.2% to about 8% and preferably from about 0.5% to about 5% by weight of the alumina on a dry basis. It has been found that halogen concentrations below these lower limits do not give the desired improvement and, on the other hand, concentrations of halogen above the upper limits adversely affect the selectivity of the catalyst, thus catalyzing side reactions to an extent greater than desired.

As hereinbefore set forth, it is essential that the platinum compound be incorporated in the alumina or alumina-halogen composite in the presence of ammonium hydroxide to obtain uniform distribution of the platinum throughout the catalyst mass. In a preferred embodiment of the present invention, the alumina, either with or without halogen, is formed into particles of uniform size and shape prior to the addition of the platinum compound. When the alumina is to be formed into particles of uniform size and shape by pilling, the wet alumina cake, with or without halogen, is dried at a temperature of from about 200° to about 500° F. for a period of from about 2 to 24 hours or more. The partially dried cake is ground and a suitable lubricant is added, such as stearic acid, rosin, hydrogenated coconut oil, graphite, etc., after which the composite is formed into pills in any suitable pelleting machine. Particularly satisfactory particles comprise cylindrical pills of a size ranging from about $\frac{1}{16}$'' x $\frac{1}{16}$'' to $\frac{1}{4}$'' x $\frac{1}{4}$'' or thereabouts. Pills of uniform size and shape may also be formed by extrusion or other suitable methods. As hereinbefore set forth, it is an essential feature of the preferred embodiment of the present invention that the pills, prior to the addition of the platinum compound, are calcined at a temperature above 1000° F. In some cases, the lubricant will be removed during the high temperature heating. In other cases as, for example, when graphite is used as the lubricant, the lubricant will not be removed during the heating step.

In accordance with the invention, the alumina or alumina-halogen particles are impregnated with a platinum compound-ammonium hydroxide solution in order to obtain even distribution of the platinum compound throughout the preformed particles. This has not been obtained in the absence of the ammonium hydroxide solution as has been clearly demonstrated by impregnating alumina pills in the presence and absence of ammonium hydroxide solution. Pills prepared in both of these methods have been treated with hydrogen sulfide to fix the platinum compound as the sulfide which is a dark color. Upon splitting open, it was observed that the pills impregnated in the presence of ammonium hydroxide solution were of the same color throughout, whereas the pills impregnated in the absence of ammonium hydroxide were of a dark color on the outside and of a light color on the inside.

A possible explanation of the benefits obtained with the evenly distributed catalyst pills is that the platinum molecules are spread throughout the pills and therefor are spaced further apart and will not result in the formation of large crystals of platinum. On the other hand, in the surface coated pills, the platinum molecules are spaced closer together and therefore may form large crystals. Another advantage to the even distribution of the platinum throughout the catalyst is that the platinum in association with hydrogen tends to reduce carbon formation and thus when the platinum is distributed evenly throughout the catalyst this effect is enhanced. On the other hand, when the platinum comprises only surface coating, the center of the pill may catalyze carbon formation because of not being able to benefit from the tendency of the platinum and hydrogen to reduce carbon formation.

Another important advantage to the even distribution of platinum throughout the catalyst from a commercial viewpoint is that a smaller volume of catalyst is required for a given plant capacity than in the case of the surface coated pills. This reduces the cost of the plant equipment by permitting the use of smaller vessels and reduced supporting structures, as well as lower catalyst shipping charges, etc. Still another advantage from a commercial viewpoint is, because of the high cost of platinum, it is advantageous to incorporate the platinum compound at the later stages of catalyst preparation in order that platinum will not be lost during subsequent handling and treating of the catalyst. Thus, it is preferred that as much of the necessary mixing, washing, filtering and heating steps be done before the platinum compound is incorporated. Further, this permits effecting the desired high temperature heating of the alumina pills at temperatures above 1000° F. without also subjecting the composite containing platinum to these high temperatures.

As hereinbefore set forth, impregnation of the alumina particles with the platinum compound is effected in the presence of an ammonium hydroxide solution and in a preferred embodiment an aqueous solution of chloroplatinic acid is commingled with ammonium hydroxide solution in proportions to form a mixed solution having a pH within the range of from about 5 to about 10 and preferably within the range of from about 8 to about 10. This mixture is then commingled with the calcined alumina-halogen pills in the preferred embodiment of the invention. As hereinbefore set forth, in another embodiment of the invention, the ammonium hydroxide solution or the chloroplatinic acid solution may be added to the alumina and the other solution subsequently added thereto.

Regardless of the order of adding the ammonium hydroxide and chloroplatinic acid solutions, a particularly advantageous method of commingling the solutions with alumina is to soak the alumina-halogen pills in an aqueous solution of chloroplatinic acid and ammonium hydroxide, and then heating the mixture. In this embodiment of the invention the alumina pills may be added to either a hot or cold solution of chloro-

platinic acid-ammonium hydroxide. In another embodiment of the invention, the alumina pills are soaked in an aqueous solution of chloroplatinic and ammonium hydroxide, and the water and residual ammonium hydroxide are removed by decantation, filtering or the like. In this embodiment of the invention, the chloroplatinic acid solution is preferably utilized as a hot solution.

After the chloroplatinic acid solution has been incorporated in the alumina pills and the water and residual ammonium hydroxide removed therefrom, the composite is dried at a temperature of from about 200° to about 500° F. for a period of about 2 to 24 hours or more and the composite is then calcined in air at a temperature of from about 500° to 1000° F. but, as hereinbefore set forth, shall not exceed 1000° F. In still another embodiment of the invention, the composite after drying may be reduced in the presence of hydrogen at a temperature of from about 500° to about 1000° F. and then calcined in the presence of air at a temperature of from about 500° to about 1000° F.

In the embodiment of the invention wherein pilling of the catalyst is not effected until after the platinum compound has been added thereto, the mass is dried at a temperature of about 200° to 500° F. for 2 to 24 hours or more and then calcined at a temperature not to exceed 1000° F. As hereinbefore set forth, after the platinum compound has been incorporated into the catalyst the composite should not be heated to a temperature in excess of 1000° F.

Although the catalyst of the present invention will have a long life, it may be necessary to regenerate the catalyst after long periods of service. The regeneration may be effected by treatment with air or other oxygen-containing gas to burn carbonaceous deposits therefrom. In general, it is preferred to control the regeneration temperature not to exceed 1000° F. and preferably the regeneration is effected at a temperature within the range of from about 600° to about 800° F.

The reforming process will be effected at a temperature within the range of from about 600° to about 1000° F., a pressure within the range of from about 50 to about 1000 pounds per square inch and at a weight hourly space velocity of from about 0.5 to about 10. The weight hourly space velocity is defined as the weight of oil per hour per weight of catalyst in the reaction zone.

Hydrocracking reactions are favored at temperatures within the range of from about 600° to about 700° F. and at pressures within the range of from about 500 to about 1000 pounds or more. Hydrocracking is defined as cracking or splitting of carbon bonds accompanied by saturation of the fragments so formed by hydrogen present in the reaction zone and, in accordance with the present invention, the hydrocracking will be selective both in quality and in quantity as hereinbefore set forth. On the other hand, aromatization reactions are favored at temperatures within the range of from about 650° to 1000° F. and at lower pressures within the range of from about 50 pounds to about 400 pounds per square inch. It is an essential feature of the present invention that the temperature, pressure and space velocity are correlated to produce the desired aromatization and selective hydrocracking. The exact temperature, pressure and space velocity to be used in any given operation will depend upon the particular gasoline fraction being treated and the particular products desired.

In one embodiment of the process, sufficient hydrogen will be produced in the reforming reaction to furnish the hydrogen required in the process and, therefore, it may be unnecessary to either introduce hydrogen from an extraneous source or to recycle hydrogen within the process. However, it usually will be preferred to introduce hydrogen from an extraneous source, generally at the beginning of the operation, and to recycle hydrogen within the process in order to be assured of a sufficient hydrogen atmosphere in the reaction zone. The hydrogen present in the reaction zone will be within the range of from about 0.5 to about 10 mols of hydrogen per mol of hydrocarbon. In some cases the gas to be recycled will contain hydrogen sulfide, introduced with the charge or liberated from the catalyst, and it is within the scope of the present invention to treat the hydrogen containing gas to remove hydrogen sulfide or other impurities before recycling the hydrogen within the process.

The process of the present invention may be effected in any suitable equipment. A particularly suitable process comprises the well known fixed bed system in which the catalyst is disposed in a reaction zone and the hydrocarbons to be treated are passed therethrough in either upward or downward flow. The products are fractionated to separate hydrogen and to recover the desired products. As hereinbefore set forth, the hydrogen preferably is recycled for further use in the process. Other suitable units in which the process may be effected include the fluidized type process in which the hydrocarbons and catalysts are maintained in a state of turbulence under hindered settling conditions in a reaction zone, the compact moving bed type in which the catalyst and hydrocarbons are passed either concurrently or countercurrently to each other, and the suspensoid type of operation in which the catalyst is carried into a reaction zone as a slurry in the hydrocarbon oil.

The following examples are introduced to further illustrate the novelty and utility of the present invention, but not with the intention of unduly limiting the same.

EXAMPLE I

A catalyst was prepared in accordance with the present invention by adding ammonium hydroxide to aluminum chloride hexahydrate to form aluminum hydrate. The resultant aluminum hydrate was washed very thoroughly in order to reduce the chloride content to below 0.1% by weight on a dry basis. This washing entailed 6 separate washes with large amounts of water containing a small amount of ammonium hydroxide and a final wash with water, with intervening filtering between washes. An aqueous solution of hydrogen fluoride was added to the washed alumina in an amount of about 0.3% by weight of alumina on a dry basis. The alumina-fluorine composite was dried at a temperature of about 340° F. for 8–10 hours in order to reduce the moisture content to about 30%. The partially dried alumina was ground, Stearotex added as lubricant, and then pilled in a Stokes pelleting machine to form cylindrical pills of ⅛" x ⅛" in size. The pills were then calcined in air at a temperature of about 932° F. for 6 hours to remove the lubricant and then further calcined at a temperature of about 1200° F for 3 hours. Concentrated ammonium hydroxide solution (30%) was added to a dilute solution of chloroplatinic acid (0.1 grams of chloroplatinic acid in 10 cc. of water). This solution

produced no precipitate but remained a clear yellow solution, having a pH of about 9. The alumina pills were soaked in the chloroplatinic acid-ammonium hydroxide solution, the quantities being controlled to form a final catalyst containing 0.3% by weight of platinum. The mixture was then heated on a steam bath, after which the catalyst was dried at 230° F. for 3 hours and calcined in air at 932° F. for 3 hours.

Another catalyst was prepared in substantially the same manner except that the final calcination in air at 932° F. was omitted and the catalyst instead was reduced in hydrogen at 932° F. for 3 hours.

Still another catalyst was prepared in substantially the same manner but was first reduced with hydrogen at 932° F. for 3 hours and then calcined in air at 932° F. for 3 hours.

These catalysts were used for the reforming of a Mid-Continent straight-run naphtha having a boiling range of from 180° to 400° F., at a temperature of about 850° F. a pressure of 500 pounds per square inch, a weight hourly space velocity of about 2 and a hydrogen to hydrocarbon ratio of 3:1. The results of these runs are indicated in the following table.

Table I

	Charge	Catalyst 1, Calcined in air	Catalyst 2, Reduced with H_2	Catalyst 3, Reduced with H_2 and calcined in air
Reformate yield, weight percent of charge.		90.6	94.4	90.7
		90.5	94.3	91.1
		90.7	95.8	90.5
F1 octane number (Research method).	34.8	86.6	79.4	85.5
		85.7	77.8	85.0
		85.8	72.7	84.8
F2 octane number (A. S. T. M. motor method).	34.6	77.8	7.18	76.8
		77.7	72.0	76.5
		77.5	70.4	76.5
Aromatics, weight percent of charge.	6.6	47.6	39.2	46.8
			31.3	46.3
		47.5	26.6	45.8

The results reported in the above table comprise three successive 20 hour test runs for each catalyst. In this way, any tendency of the catalyst to lose activity or to increase in either aromatization or hydrocracking properties is observed.

It will be noted from the above data that the catalyst calcined in air (catalyst 1) produced a reformate having a much higher octane number than that produced in the catalyst which only was reduced in hydrogen (catalyst 2). Particular attention is called to the aromatic content of the product, which it will be noted remains substantially constant with catalyst 1 but dropped from 39.2 to 26.6 with catalyst 2. It also will be noted that following the reduction in hydrogen with calcination in air restored part of the desirable properties of the catalyst as evidenced by catalyst 3.

EXAMPLE II

This example illustrates the effect of final calcination temperature. A batch of catalyst was prepared to contain 0.3% by weight of combined fluorine and 0.3% by weight of platinum. The catalyst was pilled after the platinum was incorporated therein. A portion of the pills was calcined at 932° F. for 3 hours. Another portion of the pills was calcined at 1337° F. for 3 hours. These catalysts when used for the reforming of a Pennsylvania straight-run naphtha at a temperature of about 873° F., pressure of 500 pounds per square inch, a weight hourly space velocity of about 2 and a hydrogen to hydrocarbon ation of 3:1 gave the results in Table II.

Table II

	Catalyst 4, Calcined at 932° F.	Catalyst 5, Calcined at 1337° F.
Stabilized reformate yield, Volume percent of charge	93.0	77.2
Aromatics, weight percent of charge	38.9	26.9
Percent of material boiling below 212° F., based on total liquid product	31	63

It will be noted from the data in the above table that the catalyst calcined after the platinum was composited therewith at a temperature of 1337° F. had decreased aromatization and increased hydrocracking properties as compared to the catalyst calcined at 932° F. This is illustrated in the lower yield, the decrease in aromatics and in the higher percentage of material boiling below 212° F. As set forth in the present specifications, this amount of hydrocracking is undesirable because it represents a loss of charging stock to lower boiling material and particularly to gaseous products which cannot be used in gasoline.

EXAMPLE III

Another batch of catalysts was prepared in substantially the same manner as hereinbefore set forth except that the composite of alumina and fluorine was divided into two portions. One portion was calcined at 932° F. for 3 hours and the other portion was calcined at 1337° F. for 3 hours. Platinum was thereafter composited separately with the two portions, following which the portions were separately dried, pilled and calcined at 932° F. for 3 hours. These portions were used in separate runs to reform a Mid-Continent straight-run naphtha under substantially the same conditions recited in Example II, and gave the following results.

Table III

	Catalyst 6, Calcined at 932° F.	Catalyst 7, Calcined at 1337° F.
Stabilized reformate yield, Volume percent of charge	92.5	89.6
Aromatics, weight percent of charge	44.7	44.5
F1 octane number	83.7	88.8
F2 octane number	76.6	80.1
Percent of material boiling below 212° F., based on total liquid product	28.2	39.6

From the data in the above table, it will be noted that calcination of the alumina-fluorine composite to a temperature of above 1000° F. results in a reformate of higher octane number. Although hydrocracking is moderately increased by the higher temperature calcination of the alumina-fluorine composite, aromatization is not decreased, which results in a final reformate product of higher octane number and only slightly lower yield.

EXAMPLE IV

Another batch of catalyst was prepared in substantially the same manner as hereinbefore set forth. After preparation of the alumina-fluorine pills, the batch was divided into two portions. One portion of the pills was impregnated with chloroplatinic acid-ammonium hydroxide solution and the other portion of the pills was im-

pregnated with chloroplatinic acid solution free from ammonium hydroxide. After final calcination at 932° F., hydrogen sulfide was separately passed through each of the two portions and the catalyst pills were split in half. The pills impregnated in the presence of ammonium hydroxide solution were of a uniform grayish color throughout. The pills impregnated in the absence of ammonium hydroxide solution were a grayish color on the outside but were of a lighter color in the center. This illustrates that the pills impregnated with ammonium hydroxide solution contained the platinum evenly distributed throughout and that the pills impregnated in the absence of ammonium hydroxide solution resulted only in surface coating.

EXAMPLE V

In order to show the effect of fluoride ions in alumina-platinum catalysts, two separate catalysts were prepared, one to contain no fluorine and the other to contain 1.5% fluorine. These catalysts were used in separate runs for reforming a Pennsylvania straight-run naphtha having an F2 octane number of 41.8, at a temperature of 874° F., pressure of 500 pounds per square inch and a weight hourly space velocity of about 2. The results are shown in the following table.

Table IV

	Catalyst 8, No fluorine in catalyst	Catalyst 9, Catalyst containing 1.5% fluorine
Liquid volume yield, percent of charge	96.0	82.5
F2, octane number	59.8	78.8

It will be noted that the catalyst containing fluorine yielded a reformate of 19 octane numbers higher than the catalyst containing no fluorine.

EXAMPLE VI

This example illustrates the effect of different amounts of flourine in the alumina-platinum catalysts. These catalysts were prepared to contain 1.5%, 3% and 6% fluorine and were used for the reforming of the same gasoline described in Example V and under the same conditions of operation except that the temperature was varied as shown in the following table.

Table V

	Catalyst 10, 1.5% fluorine	Catalyst 11, 3% fluorine	Catalyst 12, 6% fluorine
Reforming temperature, ° F.	874	824	755
Reformate yield, weight percent of charge	83.2	85	77.6
F2 octane number	78.8	77.4	72.4

It will be noted that the catalyst containing 1.5% and 3% fluorine gave octane numbers of 78.8 and 77.4 and yields of 83.2% and 85% respectively, whereas the catalyst containing 6% fluorine gave a much lower yield and a lower octane number gasoline.

EXAMPLE VII

The effect of chlorine content on the catalyst as shown in this example, wherein three different catalysts comprising 0.1% platinum on alumina were prepared to contain 0.5%, 1.5% and 3.5% chlorine in the final catalyst. These catalysts were used for the separate reforming of a Pennsylvania straight-run naphtha having a boiling range of from 219° to 339° F. and an F2 octane number of 41.2. The reforming was effected at 872° F., 500 pounds and a space velocity of about 2. The results of these runs are shown in the following table.

Table VI

	Catalyst 13, 0.5% chlorine	Catalyst 14, 1.5% chlorine	Catalyst 15, 3.5% chlorine
Liquid volume yield, weight percent of charge	92.3	89.5	93.4
F2, octane number	64.2	74.6	76

It will be noted that the catalyst containing 0.5% chlorine produced a reformate of 64.2 octane number. Therefore, the chloride content of the catalyst preferably is not below about 0.5% and certainly not below about 0.2%. Catalysts No. 8 and No. 9 containing higher concentrations of chlorine produced higher octane number products. However, the chlorine content should not be increased above about 8% and preferably not above about 5% because the catalyst will produce excessive hydrocracking and result in an excess of gas formation.

EXAMPLE VIII

In order to show the definite advantage to the use of a small amount of platinum in conjunction with alumina, two catalysts were prepared in substantially the same manner except that one catalyst contained 0.1% by weight of platinum composited with alumina and the other catalyst comprised alumina but contained no platinum. These catalysts were used in the reforming of a Pennsylvania straight-run naphtha having a boiling range of from 226° F. to 350° F. and an F2 octane number of 41.8, at 872° F., 500 pounds and weight hourly space velocity of about 2. The results of these runs are shown in the following table.

Table VII

	Catalyst 16, 0.1% platinum-alumina	Catalyst 17, Alumina
Liquid volume yield percent of charge	81.6	99
F2 octane number	80	50.6

It will be noted that the catalyst containing no platinum yielded a product of 50.6 octane number, whereas the platinum-containing catalyst yielded a product of 80 octane number. It is readily apparent that the 0.1% by weight of platinum exerts a definite catalytic effect.

I claim as my invention:

1. A method of manufacturing a catalyst which comprises combining a halogen with alumina in an amount of from about 0.1 to about 8% by weight of said alumina on a dry basis, forming the alumina into particles of uniform size and shape, calcining said particles at a temperature of from about 1000° to about 1400° F., commingling with the calcined particles a platinum compound-ammonium hydroxide solution in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum, and heating the composite at a temperature of from about 500 to about 1000° F.

2. The method of claim 1 further characterized in that said halogen comprises fluorine in an

amount of from about 0.1 to about 3% by weight of alumina on a dry basis.

3. The method of claim 1 further characterized in that said halogen comprises chlorine in an amount of from about 0.2 to about 8% by weight of the alumina on a dry basis.

4. A method of preparing a catalyst which comprises precipitating alumina from aluminum chloride, washing to remove chloride ions to below about 0.1% by weight of said alumina, combining fluorine with the alumina in an amount of from about 0.1 to about 3% by weight of said alumina, forming the composite into particles of uniform size and shape, calcining the particles at a temperature of from about 1000° to about 1400° F. commingling with the calcined particles a platinum compound-ammonium hydroxide solution in an amount to form a final catalyst containing from about 0.01% to about 1% by weight of platinum, and heating the composite at a temperature of from about 500° to about 1000° F.

5. A method of manufacturing a catalyst which comprises precipitating alumina from aluminum chloride, washing to remove chloride ions to below about 0.1% by weight of said alumina, adding a dilute aqueous solution of hydrogen fluoride to said alumina in an amount to form a final catalyst containing from about 0.1 to about 3% by weight of fluorine based on said alumina, pelleting the composite to form pills of uniform size and shape, calcining the pills at a temperature of from about 1000° to about 1400° F., commingling with said pills a platinum compound-ammonium hydroxide solution having a pH of from about 5 to about 10 in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum, and calcining the final composite in air at a temperature of from about 500° to about 1000° F.

6. The method of claim 5 further characterized in that said platinum compound-ammonium hydroxide solution is commingled with the alumina-fluorine pills by soaking the latter in the former and thereafter heating the same.

7. A method of manufacturing a catalyst which comprises precipitating alumina from aluminum chloride, washing to remove chloride ions to below about 0.1% by weight of said alumina, pelleting the alumina to form pills of uniform size and shape, calcining the pills at a temperature of from about 1000° to about 1400° F., adding a dilute aqueous solution of hydrogen fluoride to said pills in an amount to form a final catalyst containing from about 0.1 to about 3% by weight of fluorine based on said alumina, commingling with the calcined pills a platinum compound-ammonium hydroxide solution having a pH of from about 5 to about 10 in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum, and calcining the composite in air at a temperature of from about 500° to about 1000° F.

8. A method of preparing a catalyst which comprises precipitating alumina from aluminum chloride, washing with water containing ammonium hydroxide to remove chloride ions to below about 0.1% by weight of said alumina, adding a dilute aqueous solution of hydrogen fluoride to said alumina in an amount to form a final catalyst containing from about 0.1% to about 3% by weight of fluorine based on said alumina, drying the composite to a moisture content of about 30%, grinding the mass and adding a lubricant, pelleting to form cylindrical pills, calcining at a temperature of from about 1000° to about 1400° F., commingling with the calcined pills a platinum compound-ammonium hydroxide solution having a pH of from about 5 to about 9 in an amount to form a final catalyst containing from about 0.01% to about 1% by weight of platinum by soaking the alumina pills in said platinum compound-ammonium hydroxide solution, thereafter heating to evaporate water and residual ammonium hydroxide, and finally calcining the composite in air at a temperature of from about 500° to about 1000° F.

9. The method of claim 8 further characterized in that said composite is reduced in the presence of hydrogen at a temperature of from about 500° to about 1000° F. prior to said calcining in air.

10. A process for reforming a gasoline fraction which comprises subjecting said fraction to contact at reforming conditions with a catalyst prepared by combining a halogen with alumina in an amount of from about 0.1 to about 8% by weight of said alumina on a dry basis, forming the alumina into particles of uniform size and shape, calcining said particles at a temperature of from about 1000° to about 1400° F., commingling with the calcined particles a platinum compound-ammonium hydroxide solution in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum and heating the composite at a temperature of from about 500° to about 1000° F.

11. A process for reforming a saturated gasoline fraction which comprises subjecting said fraction to contact at reforming conditions with a catalyst prepared by precipitating alumina from aluminum chloride, washing to remove chloride ions to below about 0.1% by weight of said alumina, combining fluorine with the alumina in an amount of from about 0.1% to about 8% by weight of said alumina on a dry basis, forming the alumina into particles of uniform size and shape, calcining said particles at a temperature of from about 1000° to about 1400° F., commingling with the calcined particles a platinum compound-ammonium hydroxide solution in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum, and heating the composite in air at a temperature of from about 500° to about 1000° F.

12. A process for reforming a straight-run gasoline which comprises subjecting said fraction to contact at a temperature of from about 500° to about 1000° F., a pressure of from about 50 to about 1000 pounds per square inch and a weight hourly space velocity of from about 0.5 to about 10, in the presence of from about 0.5 to about 10 mols of hydrogen per mol of hydrocarbon, with a catalyst prepared by precipitating alumina from aluminum chloride, washing to remove chloride ions to below about 0.1% by weight of said alumina, combining fluorine with the alumina in an amount of from about 0.1% to about 3% by weight of said alumina on a dry basis, forming the composite into particles of uniform size and shape, calcining the particles at a temperature of from about 1000° to about 1400° F., commingling therewith a platinum compound-ammonium hydroxide solution in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum and heating the composite in air at a temperature of from about 500° to about 1000° F.

13. In the manufacture of a platinum-alumina catalyst wherein a halogan is combined with alumina in an amount of from about 0.1 to about 8% by weight of the alumina on a dry basis and

the alumina is impregnated with a platinum-containing solution in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum, the method which comprises forming the halogen-containing alumina into particles of uniform size and shape, calcining said particles at a temperature of from about 1000° to about 1400° F., impregnating the calcined particles with a solution of a platinum compound in the presence of ammonium hydroxide, and heating the thus impregnated particles at a temperature of from about 500° to about 1000° F.

14. In the manufacture of a catalyst comprising platinum, alumina and a combined halogen in an amount of from about 0.1 to about 8% by weight of the alumina on a dry basis, wherein the alumina is impregnated with a platinum-containing solution in an amount to form a final catalyst containing from 0.01% to 1% by weight of platinum, the method which comprises forming the alumina into particles of uniform size and shape, calcining said particles, impregnating the calcined particles with a solution of a platinum compound in the presence of ammonium hydroxide, and calcining the thus impregnated particles at a temperature not substantially in excess of about 1000° F.

15. A method of manufacturing a catalyst which comprises combining a halogen with alumina in an amount of from about 0.1 to about 8% by weight of the alumina on a dry basis, forming the alumina into particles of uniform size and shape, calcining said particles, impregnating the calcined particles in the presence of ammonium hydroxide with a solution of a platinum compound in an amount to form a final catalyst containing from about 0.01 to about 1% by weight of platinum, and heating the composite at a temperature of from about 500 to about 1000° F.

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