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METHOD OF MANUFACTURING PLATINUM-CONTAINING CATALYST

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This invention relates to a reforming process and to the manufacture of catalysts for use therein. This application is a continuation-in-part of my earlier applications Serial No. 60,381, filed November 16, 1948, now Patent No. 2,611,736, September 23, 1952, and Serial No. 142,351, filed February 3, 1950, now abandoned.

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 425° F. or more, 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 425° F. or more.

The present invention is particularly applicable to the reforming of straight run gasolines which contain naphthenic hydrocarbons, and paraffinic hydrocarbons which usually are of straight chain or slightly branched chain structure, as well as varying proportions of aromatic hydrocarbons. The invention is also applicable to the reforming of cracked gasolines and particularly thermally cracked gasoline, either alone or in admixture with straight-run gasoline. 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. Further, 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

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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.

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 propyl groups which, in the presence of hydrogen, are converted to 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, in the presence of hydrogen, 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 methyl groups which, in the presence of hydrogen, are converted to 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. 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 gasoline fraction to contact at reforming conditions with a catalyst prepared by compositing platinum with a support in the presence of a basic compound.

In a specific embodiment the present invention relates to a process for reforming a gasoline fraction which comprises subjecting said gasoline fraction to contact at reforming conditions with a catalyst prepared by compositing platinum with a support in the presence of ammonium hydroxide.

In another specific embodiment the present invention relates to a process for reforming a gasoline fraction which comprises subjecting said gasoline fraction to contact at reforming conditions with a catalyst prepared by compositing platinum with alumina in the presence of ammonium hydroxide.

In a more specific 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 an aqueous solution of a platinum compound and a water soluble basic compound in an amount to form a final catalyst containing from about 0.01% to about 1% by weight of platinum.

In another more specific 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 another 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 1100° F., a pressure of from about 50 to about 1000 pounds per square inch and weight hourly space velocity of from about 0.1 to about 20 in the presence of the catalyst as herein set forth.

In still another embodiment the present invention relates to a method of manufacturing a catalyst which comprises compositing platinum with a support in the presence of a basic compound.

In another specific embodiment the present invention relates to a method of manufacturing catalyst which comprises combining a halogen with a support in an amount of from about 0.1% to about 8% by weight of said support on a dry basis, commingling therewith an aqueous solution of a platinum compound in a water soluble basic nitrogen-containing 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 in air at a temperature of from about 500° to about 1100° F.

In still 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, forming said alumina-halogen composite into particles of uniform size and shape, calcining said particles at a temperature of from about 800° 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 resultant composite in air at a temperature of from about 500° to about 1100° 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 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 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.

Alumina is a particularly preferred support for compositing with the platinum because it appears to show improved 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 combination of alumina and low platinum concentration is a very active catalyst and also has 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 further has been found that the particular combination of alumina and platinum renders the catalyst susceptible to ready regeneration.

The novel method of compositing platinum also may be used with other supports including silica, zinc oxide, magnesia, zirconia, thoria, etc. as well as supports comprising two or more components such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-zinc oxide, silica-alumina-magnesia, silica-alumina-zirconia, silica-alumina-thoria, silica-alumina-zinc oxide, etc. The use of the basic compound in compositing platinum with the support offers improved advantages in uniformly distributing the platinum throughout the support which in turn offers advantages in the reforming process as hereinafter will be set forth in detail.

As an essential feature of the present invention, impregnation of the support must be effected in the presence of a basic compound. 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 the basic compound, uneven distribution of the platinum in or on the support 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 a basic com-

pound, even distribution of the platinum throughout the support is obtained.

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

It is understood that any suitable source of platinum may be used in accordance with the present invention. Chloroplatinic acid generally is preferred because it is more readily available. Solutions of other platinum-containing compounds may be employed including those of ammonium platinum chloride, trimethylbenzyl ammonium platinum chloride, tetramino platino chloride, ammonium platino nitrate, dinitro diamino platinum, etc. It is understood that, when desired, other than aqueous solutions may be employed and this is particularly useful where the platinum compound is not readily water soluble.

As hereinbefore set forth, it is an essential feature of the present invention that the impregnation of the support with platinum is effected in the presence of a basic compound. The preferred basic compound is a nitrogen containing water soluble basic compound. The basic compound should not introduce undesirable impurities into the final catalyst. A preferred basis compound for use in accordance with the present invention comprises ammonium hydroxide. Other basic compounds comprise aqueous solutions of organic amino compounds such as the alkylene polyamines including ethylene diamine, propylene triamine, butylene tetramine, etc., mono-amino compounds including methyl amine, ethyl amine, diethyl amine, triethyl amine, propyl amine, dipropyl amine, butyl amine, aniline, etc., alkanol amines, including ethanol amine, propanol amine, butanol amine, diethanol amine, triethanol amine, etc. Other satisfactory organic amino compounds include hexamethylene tertramine, hexamethylene diamine, etc.

Another suitable class of basic compounds which may be used in accordance with the present invention comprises basic ammonium compounds including ammonium carbonate, ammonium bicarbonate, ammonium carbamate, ammonium citrate, ammonium aluminate, ammonium propionate, ammonium butyrate, etc. In some cases, it may be desired to commingle ammonia with these solutions in order to insure definite basicity. As another alternative but not necessarily equivalent method, ammonium nitrate, ammonium acetate, aluminum nitrate, aluminum acetate, etc. may be employed in admixture with ammonium hydroxide in a sufficient concentration to form a basic solution. It is understood that the various basic compounds are not necessarily equivalent. In any event, the basic compound employed must not leave an undesired residue on the catalyst.

The use of a basic compound is differentiated from the use of an acidic compound as, for example, ammonium chloride. Ammonium chloride cannot be used because, upon commingling of ammonium chloride with chloroplatinic acid, a precipitate of ammonium chloroplatinate is obtained. Even upon heating or upon the addition of a basic compound, the precipitate will not be dissolved to form a clear solution. However, in some cases, both the addition of a basic compound and heating will dissolve the precipitate to form a clear solution and, in such cases, the use of ammonium chloride may be employed in conjunction with both the basic compound and heating.

With proper selection of the chloroplatinic acid solution and of a basic ammonium compound 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 a hydrolysis product of $[Pt(NH_3)_2Cl_2]Cl_2$. In any event it is apparent that the clear solution formed upon the mixing of a basic ammonium compound solution with chloroplatinic acid solution is different from the ammonium chloroplatinate precipitate formed upon the addition of ammonium chloride to chloroplatinic acid solution. If ammonium chloroplatinate is formed, as hereinbefore set forth, or due to the use of a too highly concentrated solution of chloroplatinic acid, the ammonium chloroplatinate 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.

In a preferred embodiment of the present invention, the final catalyst contains halogen in a specific concentration. It has been found, and will be shown in the following examples, that the presence of halogen 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 support and/or platinum, and thereby serves to improve the final catalyst.

While any of the halogens will serve to effect improved results, fluorine is particularly preferred. Next in order is chlorine, while bromine and iodine 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 a preferred embodiment of the present invention the final composite of platinum-support or platinum-combined halogen-support is calcined, preferably in the presence of an oxygen-containing gas, particularly air, at a temperature of from about 500° to about 1100° F. for a period of from about 1 to 12 hours or more. Calcination in the presence of air appears to result in a final gasoline product of higher octane number than is obtained when the catalyst is calcined only 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 the calcination being

effected at a temperature of from about 500° to about 1100° F.

In one embodiment of the invention the support is formed into particles of uniform size and shape prior to compositing the platinum therewith. In this embodiment of the invention, the particles of uniform size and shape are subjected to calcination at a temperature of above about 800° F. and preferably within the range of from about 1000° to about 1400° F. for a period of from about 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 should not be heated at a temperature above about 1100° F. and preferably is calcined in air at a temperature of from about 500° to about 1100° F. for a period of from about 1 to 12 hours or more as hereinbefore set forth. In another embodiment of the invention the platinum is composited with the support while the latter is in a wet condition or after only partial drying thereof. In still another embodiment of the invention, the support may be formed into particles of uniform size and shape and the platinum is composited therewith before the support is subjected to partial or substantially complete drying.

A preferred method of preparing alumina is to commingle a suitable reagent, such as ammonium hydroxide, ammonium carbonate, etc. with 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. 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 chlorine 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 chlorine is obtained from the original aluminum chloride and is retained in the alumina, thus avoiding the necessity of adding the halogen in a later step of catalyst preparation. However, it generally is difficult to control the washing procedure to retain exactly the desired amount of halogen and, for this reason, it usually is preferred to wash the alumina to remove substantially all of the chlorine and thereafter add the halogen in a controlled amount. The addition of the halogen 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 chlorine 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 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, when added, is introduced 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 from about 2 to 24 hours or more. In one embodiment 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/or platinum addition may be effected prior to forming the composite into particles of uniform size and shape.

Silica may be prepared by reacting a suitable acid such as sulfuric acid, hydrochloric acid, etc. with an alkali metal silicate and particularly water glass under conditions to precipitate silica. In another embodiment of the invention the silica may be prepared as substantially spheroidal gel particles by dropping a suitable mixture of acid and alkali metal silicate into a bath of water immiscible suspending medium, such as hydrocarbon oil, the depth and temperature of the suspending medium being controlled so that droplets form into spheroidal particles during passage through the suspending medium. In one embodiment a layer of water may be disposed beneath the oil suspending medium, and the spherical particles may be withdrawn by means of a circulating stream of water from the forming zone into suitable washing, drying and/or calcining equipment as desired. When the support comprises other metal oxides as hereinbefore set forth, they may be prepared in any suitable manner, including the formation of spherical particles. In another embodiment, when the support comprises two or more components, they may be prepared by separate, successive or conjoint precipitation or gelation. It is understood that the detailed description set forth in connection with the preparation and further handling of alumina also may apply to the other supports.

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 support 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 generally is 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 in the finished catalyst will be within the range of from about 0.1% to about 8% by weight of the support on a dry basis. Fluorine 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 support on a dry basis. Chlorine 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 support on a dry basis. It appears 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 support in the presence of a basic compound to obtain uniform distribution of the platinum throughout the catalyst mass. In one embodiment of the present invention the support, either with or without halogen, is formed into particles of uniform size and shape prior to the addition of the platinum compound. When the support is to be formed into particles of uniform size and shape by pilling, the support, 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, the pills, prior to the addition of the platinum compound, may be calcined at a temperature above 800° 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 separate high temperature heating step may be omitted, and the effective heat treatment of the catalyst may be obtained in the plant before or during processing of the hydrocarbons.

In accordance with the invention, the support is impregnated with a platinum compound-basic compound 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 therefore 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 the 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. As applied to the impregnation of preformed particles, 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, much of the necessary mixing, washing, filtering and heating steps is done before the platinum compound is incorporated. Further, this permits effecting the desired high temperature heating of the support particles at temperatures above 1100° F. without also subjecting the composite containing platinum to these high temperatures.

As hereinbefore set forth, impregnation of the support with the platinum compound is effected in the presence of a basic compound solution and, in a preferred embodiment, an aqueous solution of chloroplatinic acid is commingled with a basic compound 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 support in the manner hereinbefore set forth or, in another embodiment of the invention, the basic compound solution or the chloroplatinic acid solution may be added to the support and the other solution subsequently added thereto.

Regardless of the order of adding the basic compound and chloroplatinic acid solutions, a particularly advantageous method of commingling the solutions with the support particles is to soak the support or the support-halogen particles in an aqueous solution of chloroplatinic acid and basic compound, and then heating the mixture. In this embodiment of the invention the particles may be added to either a hot or cold solution of chloroplatinic acid-basic compound. In another embodiment of the invention, the particles are soaked in an aqueous solution of chloroplatinic acid and basic compound, and the water and residual basic compound are re-

moved 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 support and the water and residual basic compound removed therefrom, the composite 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, and the composite is then calcined in air at a temperature of from about 500° to about 1100° 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 1100° F. and then calcined in the presence of air at a temperature of from about 500° to about 1100° 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 a period of from about 2 to 24 hours or more and then calcined at a temperature not to exceed 1100° 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 1100° 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 1100° F., a pressure within the range of from about 50 to about 1000 pounds or more per square inch and at a weight hourly space velocity of from about 0.1 to about 20. 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 about 1100° 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 generally will be within the range of from about 0.1 to about 10 mols of hydrogen per mol of hydrocarbon. In some cases the gas available for recycling 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.

While the catalysts of the present invention are particularly desirable for use in reforming processes, it is understood that these catalysts may be used in any process for which platinum is a catalyst. These catalysts also may be effective for effecting hydrogenation of unsaturated aliphatic hydrocarbons such as monoolefins, diolefins, etc. to form the corresponding saturated hydrocarbons, hydrogenation of unsaturated cyclic hydrocarbons, hydrogenation of unsaturated ketones, alcohols, acids, etc. Further, these catalysts may be useful for effecting the cracking of normally gaseous or normally liquid hydrocarbons to produce lower boiling hydrocarbons, dehydrogenation of normally gaseous or normally liquid organic compounds to form the corresponding unsaturated compounds, etc. Other reactions in which these catalysts may find usefulness include oxidation as, for example, oxidation of olefins to form the corresponding oxides, such as the oxidation of ethylene to ethylene oxide, propylene to propylene oxide, etc., oxidation of alcohols, ketones, etc. These and other oxidation reactions per se are well-known in the art and it is within the scope of the present invention to effect these reactions in the presence of these catalysts. In reactions involving hydrogenation, oxidation or condensation, it is preferred that the halogen content of the catalyst be within the lower limits of the ranges hereinbefore specified in order to minimize side reactions.

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 catalyst particles are maintained in a state of turbulence under hindered settling conditions in a reaction zone, the compact moving bed type in which particulated catalyst and the hydrocarbons are passed either concurrently or countercurrently to each other, and the suspensoid type of operation in which particulated catalyst is carried into 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 hy-

droxide 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 six 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 the 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, stearic acid added as lubricant, and then pilled in a Stokes pelleting machine to form cylindrical pills of ⅛'' x ⅛'' in size. The pills were 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 gram of chloroplatinic acid in 10 cc. of water) in proportions to form a mixture having a pH of about 9. This solution produced no precipitate but remained a clear yellow solution. 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.

This catalyst was used in a series of three runs 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 molal ratio of 3:1. The results of these runs are indicated in the following table.

Table 1

	Days	Charge	Catalyst 1
Reformate yield, weight percent of charge	1		90.6
	2		90.5
	3		90.7
F1 octane number (Research Method)	1		86.6
	2	34.8	85.7
	3		85.8
F2 octane number (A. S. T. M. Motor Method)	1		77.8
	2	34.6	77.7
	3		77.5
Aromatics, weight percent of charge	1		47.6
	2	6.6	
	3		47.5

It will be noted from the above data that catalyst 1 produced a reformate having a high octane number and of high aromatic content.

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 were used for the reforming of a Pennsylvania straight-run naphtha at a temperature of about 873° F., a pressure of 500 pounds per square inch, a weight hourly space velocity of about 2 and a hydrogen to hydrocarbon molal ratio of 3:1, and gave the results reported in Table 2.

	Catalyst 2, Calcined at 932° F.	Catalyst 3, Calcined at 1,337° 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 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 impregnated with chloroplatinic acid solution in the absence of 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 IV

In order to show the effect of fluorine 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., a pressure of 500 pounds per square inch and a weight hourly space velocity of about 2 in the presence of hydrogen. The results are shown in the following table:

Table 3

	Catalyst 4, No fluorine in catalyst	Catalyst 5, 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 V

This example illustrates the effect of different amounts of fluorine 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 IV and under the same conditions of operation except that the temperature was varied as shown in the following table:

Table 4

	Catalyst 6, 1.5% fluorine	Catalyst 7, 3% fluorine	Catalyst 8, 6% fluorine
Reforming temperature, ° F	874	824	755
Reformate yield, wt. 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 VI

The effect of chlorine content on the catalyst is 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 in the presence of hydrogen. The results of these runs are shown in the following table:

Table 5

	Catalyst 9, 0.5% chlorine	Catalyst 10, 1.5% chlorine	Catalyst 11, 3.5% chlorine
Liquid volume yield, wt. 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 chlorine content of the catalyst preferably is not below about 0.5% and certainly not below about 0.2%. Catalysts No. 10 and 11 containing higher concentrations of chlorine produced higher octane number products. However, the chlorine content should not be increased above about 3% and preferably not above about 5% because the catalyst will produce excessive hydrocracking and result in an excess of gas formation.

EXAMPLE VII

A catalyst may be prepared in substantially the same manner as described in Example I, but in place of using a chloroplatinic acid-ammonium hydroxide solution, a chloroplatinic acid-ethylene diamine solution may be employed to impregnate the alumina-halogen pills. The platinum will be evenly distributed throughout the alumina in contrast to surface impregnation obtained in the absence of the ethylene diamine.

EXAMPLE VIII

A silica-platinum catalyst may be prepared by commingling sulfuric acid with water glass and dropping the resultant mixture into a bath of hydrocarbon oil maintained at substantially atmospheric temperature. A circulating stream of water is positioned beneath the bath of oil and the silica spheres are transported to a washing zone wherein soluble impurities are removed. The spheres may be soaked in an aqueous hydrochloric acid solution in order to introduce 0.5% by weight of chlorine based on the dry silica spheres. The spheres are then dried at a temperature of 350° F. for 16 hours and calcined at a temperature of 1200° F. for 4 hours. The spheres then may be soaked in a clear chloroplatinic acid-ammonium hydroxide solution, the quantities being controlled to form a final catalyst containing 0.2% by weight of platinum. The composite then is dried at 250° F. for 6 hours and calcined at 950° F. for 3 hours.

EXAMPLE IX

A catalyst may be prepared in substantially the same manner as described in Example VIII but in place of using a chloroplatinic acid-ammonium hydroxide solution a chloroplatinic acid-propylene triamine solution may be used to impregnate the silica spheres. The platinum will be evenly distributed throughout the silica in contrast to surface impregnation obtained in the absence of the basic compound.

EXAMPLE X

A silica-alumina composite is prepared and formed into particles of uniform size and shape. The particles are calcined at a temperature of 1100° F. for 3 hours and then are soaked in an aqueous solution comprising chloroplatinic acid and ammonium carbamate. The platinum concentration is controlled to comprise 0.4% by weight of the final catalyst.

EXAMPLE XI

A silica-magnesia composite is prepared by acidifying water glass with sulfuric acid to form silica gel, washing to remove soluble impurities, commingling therewith a slurry of magnesium oxide and intimately mixing the same to form a silica-magnesia composite. An aqueous solution of ammonium hydroxide is commingled with a solution of ammonium platino nitrate, and the resultant mixture is added to the wet mix of silica-magnesia with intimate stirring, following which excess solution is separated, and the resultant mass is dried at a temperature of 350° F. for 12 hours and then calcined at a temperature of 932° F. for 4 hours.

It will be found that impregnating the silica-magnesium support in the presence of the basic compound results in uniform distribution of the platinum throughout the support in contrast to surface coating obtained when the basic compound is not employed.

EXAMPLE XII

As hereinbefore set forth, the basic compound preferably comprises a nitrogen-containing basic compound. Sodium carbonate is undesirable as will be shown in this example. Two catalysts comprising alumina, 0.3% fluorine and 0.3% platinum were prepared in substantially the same manner except that a chloroplatinic acid-ammonium hydroxide solution was used as the impregnating medium in one case (catalyst 12) and a

chloroplatinic acid-sodium carbonate solution was used as the impregnating medium in the other case (catalyst 13).

When used for the reforming of different samples of a naphtha, these catalysts gave the results shown in the following table:

Table 6

	Catalyst 12 (Ammonium hydroxide)	Catalyst 13 (Sodium carbonate)
Liquid volume yield, percent of charge	89.8	94.3
F2 octane number	79.3	55.5

It will be noted that the catalyst prepared using sodium carbonate (catalyst No. 12) yielded a product of only 55.5 octane number, whereas the catalyst prepared using ammonium hydroxide (catalyst No. 13) yielded a product having an octane number of 79.3.

EXAMPLE XIII

This example compares the results obtained in reforming operations utilizing different catalysts prepared in the same manner but in one case using chloroplatinic acid-ammonium hydroxide solution (catalyst 14) as the impregnating medium and in the other case using chloroplatinic acid without ammonium hydroxide (catalyst 15).

Different samples of the same gasoline were used as the charging stock for these reforming operations. The reforming in both cases was effected at a temperature of about 850° F., a pressure of 500 pounds per square inch and a space velocity of 2, in the presence of hydrogen in a molal ratio to hydrocarbon of about 3.2.

With platinum concentration of 0.3% by weight in each case, catalyst No. 14 prepared through the use of ammonium hydroxide gave a reformate having an F1 clear octane number of 86.2. Catalyst No. 15 prepared without the ammonium hydroxide gave an F1 clear octane number of 80.4. Thus it is seen that the use of ammonium hydroxide resulted in a reformate of 5.8 octane numbers higher than the catalyst prepared without the ammonium hydroxide.

EXAMPLE XIV

In another series of reforming runs in a manner similar to that described in Example XIII but with catalysts containing 0.1% by weight of platinum in each case, catalyst No. 16 prepared through the use of ammonium hydroxide gave a reformate of 5.9 octane numbers higher than catalyst No. 17 prepared without the ammonium hydroxide medium and in the other case using chloroplatinic acid without ammonium hydroxide (catalyst 19).

Different samples of the same gasoline were used as the charging stock for these reforming operations. The reforming in both cases was effected at a temperature of about 850° F., a pressure of 500 pounds per square inch and a space velocity of 2, in the presence of hydrogen in a molal ratio to hydrocarbon of about 3.2.

With platinum concentration of 0.3% by weight in each case, catalyst No. 18 prepared through the use of ammonium hydroxide gave a reformate having an F1 clear octane number of 86.2. Catalyst No. 19 prepared without the ammonium hydroxide gave an F1 clear octane number of 80.4 Thus it is seen that the use of ammonium hydroxide resulted in a reformate of 5.8 octane numbers higher than the catalyst prepared without the ammonium hydroxide.

EXAMPLE XV

In another series of reforming runs in a manner similar to that described in Example XIV but with catalysts containing 0.1% by weight of platinum in each case, catalyst No. 20 prepared through the use of ammonium hydroxide gave a reformate of 5.9 octane numbers higher than catalyst No. 21 prepared without the ammonium hydroxide.

I claim as my invention:

1. A method of manufacturing a catalyst which comprises impregnating a porous support with a solution of a platinum compound in contact with a basic compound selected from the group consisting of basic ammonium salts and organic amino compounds, and calcining the thus impregnated support.

2. A method of manufacturing a catalyst which comprises impregnating a porous support with a solution of a platinum compound in contact with a basic organic amino compound, and calcining the thus impregnated support.

3. A method of manufacturing a catalyst which comprises impregnating a porous support with a solution of a platinum compound in contact with an amine, and calcining the thus impregnated support.

4. A method of manufacturing a catalyst which comprises impregnating a porous support with a solution of a platinum compound in contact with an alkylene polyamine, and calcining the thus impregnated support.

5. A method of manufacturing a catalyst which comprises impregnating a porous support with a solution of a platinum compound in contact with an alkanol amine, and calcining the thus impregnated support.

6. A method of manufacturing a catalyst which comprises impregnating a porous support with a solution of a platinum compound in contact with ammonium carbonate, and calcining the thus impregnated support.

7. A method of manufacturing a catalyst which comprises impregnating a porous support with a solution of a platinum compound in contact with ammonium carbamate, and calcining the thus impregnated support.

8. A method of manufacturing a catalyst which comprises combining a halogen with porous alumina in an amount of from about 0.1% to about 8% by weight of said alumina on a dry basis, forming the composite into particles, calcining said particles, impregnating the calcined particles with a solution of a platinum compound in contact with a basic compound selected from the group consisting of basic ammonium salts and organic amino compounds, and calcining the thus impregnated particles.

9. The method of claim 8 further characterized in that said basic compound is an amine.

10. A method of manufacturing a catalyst which comprises commingling with porous alumina a solution of a platinum compound and a basic compound selected from the group consisting of basic ammonium salts and organic amino compounds, said platinum compound being in an amount to form a final catalyst containing from about 0.01% to about 1% by weight of platinum, and calcining the resultant mixture.

11. A method of manufacturing a catalyst which comprises combining a halogen with a porous support in an amount of from about 0.1% to about 8% by weight of said support on a dry basis, commingling therewith a solution of a platinum compound and a basic compound selected

from the group consisting of basic ammonium salts and organic amino compounds, said platinum compound being in an amount to form a final catalyst containing from about 0.01% to about 1% by weight of platinum, and calcining the resultant mixture.

12. The method of claim 11 further characterized in that said halogen comprises fluorine in an amount of from about 0.1% to about 3% by weight of the suport on a dry basis.

13. The method of claim 11 further characterized in that said halogen comprises chlorine in an amount of from about 0.2% to about 8% by weight of the support on a dry basis.

14. The method of claim 11 further characterized in that said support comprises silica.

15. The method of claim 11 further characterized in that said support comprises silica and a metal oxide.

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