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REFORMING CATALYST

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This invention relates to a reforming process for obtaining gasoline of high octane number. More particularly, the present invention is directed to catalytic reforming carried out in the presence of an improved platinum-containing catalyst. The invention is further directed to the manufacture of said catalyst.

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

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

Controlled or selective cracking is highly desirable during reforming since such will result in a product of improved anti-knock characteristics. As a general rule, the lower molecular weight hydrocarbons exhibit a higher octane number, and a gasoline product of lower average molecular weight will usually have a higher octane number. The splitting or cracking of carbon to carbon linkages must, however, be selective and should be such as not to result in substantial decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons. Uncontrolled cracking, moreover, generally results in rapid formation and deposition on the catalyst of large quantities of a carbonaceous material generally referred to as "coke." The production of coke not only results in decreased yields of gasoline but the deposition thereof on the catalyst surface diminishes or destroys its catalyzinng effect and results in shorter processing periods with the accompanying necessity of frequent regeneration by burning the coke therefrom. In those instances

where the activity of the catalyst is destroyed, it is necessary to shut down the unit, remove the deactivated catalyst, and replace it with new catalyst. Such practice obviously is time-consuming and inefficient, imparting a greater overall expense to the reforming operation.

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

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

In accordance with the present invention, a process for reforming a hydrocarbon mixture boiling in the gasoline range is provided which comprises subjecting the same to contact at reforming conditions with a catalyst prepared by pretreating alumina with gaseous carbon dioxide, and thereafter, while maintaining the alumina so treated out of contact with air, effecting impregnation thereof with a solution of a platinum compound present in an amount such that, after drying and calcining, the final catalyst contains from about 0.05 to about 5 and preferably from about 0.1 to about 2 percent by weight of platinum.

The instant invention further provides a method of manufacturing a catalyst which comprises contacting an alumina support with gaseous carbon dioxide, impregnating the support, without intermediate contact thereof with air, with a solution of a platinum compound in an amount to form a final catalyst containing from about 0.05 to about 5 and preferably from about 0.1 to about 2 percent by weight of platinum and thereafter heating the composite at a temperature of from about 500° F. to about 1000° F.

A number of platinum-containing reforming catalysts have heretofore been proposed wherein the platinum is impregnated on an alumina base by bringing the same into contact with a solution of a suitable platinum compound and subsequently drying and calcining in an atmosphere of air or hydrogen. The present invention is based on the discovery that exceptionally good catalysts may be prepared by pretreating the alumina support with gaseous carbon dioxide and maintaining the alumina support out of contact with air while impregnating with a solution of a platinum compound. Reforming with catalysts so prepared affords a distinct advantage, as will be apparent from data hereinafter set forth, over reforming with catalysts which have not been subjected to the aforesaid pretreatment with gaseous carbon

dioxide. This invention accordingly represents an improvement in catalyst manufacture and in catalytic reforming.

In order to obtain the advantages of the present invention, a particular type of supporting material must be composited with the platinum. Such supporting material consists essentially of alumina. In some instances, it is desirable to employ an alumina support having a small amount of halogen incorporated therein. It has been previously noted that alumina possesses advantages for use as a supporting material for platinum, and it has been postulated that such advantages are apparently due to some peculiar association of alumina with platinum either as a chemical combination or as a physical association. Whether or not such postulation is correct, it has heretofore been established that the specific combination of alumina and platinum has several advantages over platinum deposited on other supporting materials. Thus, alumina has been known to impart stability to the platinum in subsequent aging, thereby permitting use of the catalyst over an extended period of time in reforming operations without necessitating regeneration.

The carrier or support employed herein for the platinum is a porous alumina. This alumina desirably has a surface area greater than about 10 square meters per gram and preferably in excess of 30 square meters per gram and may extend up to 500 square meters per gram or more. The term "surface area" as used herein designates the surface area of the alumina as determined by the adsorption of nitrogen according to the method of Brunnauer et al., Journal American Chemical Society 60, 309 et. seq. (1938).

The alumina base may comprise an alumina precipitate, an alumina gel either in the form of a gelatinous precipitate or a hydrogel or a mixture of precipitate and hydrogel. The alumina may be employed in massive form but generally will be in the form of a powder or in particle form, either irregularly shaped or uniformly shaped as beads, cubes, tablets, extruded pellets, and the like. The size of the dried alumina particles will generally be in the range from 3 to 325 mesh (Tyler). In the preparation of spheroidal alumina gel particles, an alumina hydrosol is prepared by intimate admixture of suitable reactants and the hydrosol is introduced in the form of globules to a water-immiscible medium, the depth and temperature of which is controlled so that the hydrosol globules set to spheroidal particles of hydrogel during passage through said medium. The resulting hydrogel particles are thereafter withdrawn from the forming zone and conducted to suitable washing, drying and/or calcining equipment as described. Alumina, in the form of a precipitate, may be prepared by adding a suitable reagent such as ammonium hydroxide or ammonium carbonate to an aluminum salt such as aluminum chloride, aluminum nitrate, aluminum acetate, etc. in an amount to form aluminum hydroxide which, upon drying, is converted to alumina. After the alumina has been formed, it is generally washed to remove soluble impurities. Washing procedures ordinarily involve washing with water, either in combination with filtration or as separate operations. It has been found that filtration of the alumina is improved when the wash water contains a small amount of ammonium hydroxide. The exent of washing will depend to some extent on the nature of the reactants initially employed in preparation of the alumina precipitate. Thus, as noted hereinabove, it is sometimes desirable that the alumina support contain a small amount of halogen. When aluminum chloride is used as one of the initial reactants, chloride ions are contained in the resulting unwashed alumina. In such instances, the extent of washing may be controlled to remove the bulk of the chloride ions but to retain a small amount of chloride, generally in the range of 0.1% to 8% by weight of the alumina on a dry basis. Using such procedure, the need for addition of halogen ions in a later step of the catalyst preparation is avoided. It is generally preferred, however, to wash the alumina precipitate substantially free of chloride or other halogen ions and to subsequently add such ions to the alumina either before impregnation with the platinum compound or to impregnate the alumina with a halogen containing platinum compound such as chloroplatinic acid which serves to simultaneously introduce platinum and chloride ions to the alumina. In some cases, it may be desirable to add a halogen to the alumina, for example, fluorine, and thereafter to impregnate the halogen-containing alumina with chloroplatinic acid. In such case, the ultimate catalyst would contain two halogens, i.e. fluorine and chlorine.

After washing and filtration, the alumina is obtained as a wet cake. Such cake is dried to reduce the same to a moisture content of less than 50%, which generally requires drying at a temperature in the approximate range of 200 to 500° F. for a period of 2 to 24 hours or longer. The dried cake may then be granulated and calcined in air at a temperature between about 500° F. and about 1000° F. for a period of 1 to 12 hours or longer. The calcined granules may thereafter be ground to suitable mesh size and pretreated with gaseous carbon dioxide as hereinafter described. Alternatively, the dried cake may be formed into particles of uniform size and shape before calcining as by pelleting, casting, extrusion or other suitable methods and thereafter calcined and treated with gaseous carbon dioxide. Halogen, if added before impregnation of the alumina may be introduced at various stages of the catalyst preparation. Thus, halogen may be added to the alumina either before or after drying the same and either before or after the alumina has been formed into desired shape.

Halogen should be added in a form which will readily react with the alumina in order to obtain the desired results without leaving undesired deposits on the catalyst. It is preferred, in accordance with the present invention, to introduce halogen simultaneously with the platinum after the alumina has undergone treatment with carbon dioxide. Thus, it is a preferred embodiment of the invention to pretreat the alumina base with gaseous carbon dioxide and to thereafter impregnate the alumina in a gaseous carbon dioxide atmosphere with a solution of a halo-platinum acid such as chloroplatinic acid. However, as noted hereinabove, the alumina may have halogen added thereto prior to impregnation with the platinum compound. In such case, the alumina may suitably be contacted with a hydrogen halide such as hydrogen fluoride, hydrogen chloride, hydrogen bromide and/or hydrogen iodide. These materials are preferably employed as aqueous solutions. The ammonium salts of these acids may also be employed. The amount of halogen introduced into the alumina either before and/or during impregnation with the platinum compound is such that the ultimate catalyst will contain between about 0.1 and about 8 percent by weight of the alumina on a dry basis.

It is an essential feature of the present invention that the alumina base be preterated with gaseous carbon dioxide prior to impregnation with a solution of a platinum compound. The alumina base either with or without halogen is dried to a water content preferably of less than 30 percent by weight. It is particularly preferred that the alumina base, after drying, be calcined before contact thereof with gaseous carbon dioxide. The dried and/or calcined alumina is thereafter, in accordance with the process of this invention, treated with gaseous carbon dioxide. Such treatment is effected under ordinary temperature conditions utilizing a carbon dioxide pressure in the range of 0 to 50 p.s.i.g. The alumina is generally treated with carbon dioxide for a period between about one minute and about 24 hours and more usually between about one minute and about 3 hours. It is to be noted that the time of gas treatment and the gauge pressures set forth above are not considered critical, it being only necessary that the alumina base be exposed to a gaseous

carbon dioxide atmosphere for a sufficient period of time and under sufficient pressure to become substantially saturated. The gas initially contained in the pores of the alumina base, which will ordinarily be air, may be replaced by sweeping the alumina particles with gaseous carbon dioxide for a sufficient period of time to replace substantially all of the air in the pores of the alumina with carbon dioxide. It is generally preferred, however, to subject the porous alumina base to a vacuum, thereby removing the air or other gas contained therein and subsequently to contact the evacuated particles with gaseous carbon dioxide. The alumina, after treatment with carbon dioxide, is thereafter impregnated with a solution of a suitable platinum compound. It is an essential feature of the present invention to maintain the pretreated alumina out of contact with air while the impregnation with platinum compound is carried out. In a preferred embodiment of the invention, the alumina, after pretreatment, is maintained in an atmosphere of gaseous carbon dioxide during the subsequent impregnation. Desirably, the alumina which has undergone pretreatment with gaseous carbon dioxide should be brought into contact with the impregnating solution of platinum compound immediately after such pretereatment to insure the optimum results of this invention.

A particularly effective method of impregnating the carbon dioxide treated alumina comprises the use of an aqueous solution of chloroplatinic acid. Thus, in a preferred embodiment of the invention, an aqueous solution of chloroplatinic acid is commingled with the carbon dioxide treated alumina particles and the resulting mixture is permitted 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. This period of contact will generally be in the approximate range of 2 to 48 hours and more usually between about 16 and about 24 hours. While an aqueous solution of chloroplatinic acid is generally preferred as the impregnating solution, it will be realized that the chemically equivalent solution of platinic chloride in dilute aqueous hydrochloric acid may likewise be used. Platinic chloride is derived from metallic platinum by aqua regia as the usual starting point for the preparation of other platinum salts and while other platinum salts may be employed as impregnating solutions in the preparation of platinum catalysts, it is ordinarily less expensive and therefore more desirable to proceed from platinic chloride or chloroplatinic acid. Experience has shown that alumina base catalysts prepared from chloroplatinic acid hold most tenaciously a substantial portion of the chloride of the impregnating solution which remains on the finished catalyst even after drying and calcining. Other suitable halo-platinum acids which may be employed as impregnating solutions include bromoplatinic acid, chloroplatinous acid, and bromoplatinous acid. Solutions of other platinum-containing compounds which may be employed for impregnation include those of ammonium platinum chloride, trimethylbenzyl ammonium platinum chloride, tetramino platino chloride, ammonium platino nitrate, dinitro diamino platinum. In those instances where the platinum impregnating solution does not serve to simultaneously introduce halogen into the alumina, it will be understood that the alumina undergoing impregnation has previously been treated as described hereinabove with a halogen compound to incorporate therein an amount of halogen in the range of about 0.1 to about 8 percent by weight of the alumina on a dry basis. It will be 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.

The resulting composite of alumina, platinum compound, and combined halogen is dried at a temperature of from about 200° F. to about 500° F. for a period of about 2 to 24 hours or longer and thereafter the composite is calcined in the presence of an oxygen-containing gas such as air at a temperature of from about 500° F. to about 1000° F. for a period of 1 to 12 hours or more. If desired, the composite, after drying, may be reduced in the presence of hydrogen and thereafter calcined in the presence of air, both the reduction and calcination being carried out at temperatures between about 500° F. and about 1000° F. The use of temperatures of greater than 1000° F. in treating the final composite containing platinum is to be avoided.

As hereinabove set forth, it is essential to the success of the present invention that the alumina be pretreated with gaseous carbon dioxide before undergoing impregnation with the solution of platinum compound. The resulting catalyst has an improved activity in the reforming of petroleum hydrocarbons boiling in the gasoline range over catalysts prepared by impregnating the alumina in the absence of carbon dioxide pretreatment. The exact reason for the unexpected marked improvement in reforming activity is not clearly understood. However, without being limited by any theory, it would appear that the carbon dioxide pretreatment of the alumina prevents adsorption of platinum during impregnation of the alumina with the solution of platinum compound and that, after the platinum becomes uniformly dispersed, the carbon dioxide is removed during subsequent heating or by reducing the pressure, and the platinum is adsorbed in place. Thus, the platinum being adsorbed remains fixed during subsequent drying and calcining. Observation of the catalyst particles produced by the method described herein has shown the platinum to be uniformly dispersed. On the other hand, corresponding catalysts impregnated without pretreatment with gaseous carbon dioxide have shown platinum shells. The latter indicates that the platinum was adsorbed by the outer surface of alumina during impregnation when no pretreatment with carbon dioxide was employed.

The catalyst prepared in accordance with the process of this invention consists essentially of alumina having a content of combined halogen of between about 0.1 percent and about 8 percent by weight of the alumina on a dry basis. When the halogen is fluorine, the amount thereof will generally be in the approximate range of about 0.1 to about 3 percent by weight of the alumina on a dry basis. When the halogen is chlorine, the amount thereof is preferably in the range of about 0.5 percent to about 5 percent by weight of the alumina on a dry basis. The platinum content of the ultimate catalyst is generally within the approximate range of 0.05 percent to about 5 percent, and preferably between about 0.1 percent and about 2 percent, by weight of the alumina on a dry basis.

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

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

boiling point of between about 350° F. and about 425° F.

Reforming in accordance with the present invention may be carried out in any suitable equipment. A particularly feasible process comprises a fixed bed system in which the catalyst is contained in a reaction zone and the hydrocarbons to be treated are passed therethrough. The resulting products are fractionated to separate hydrogen and to recover the desired products. The recovered hydrogen is preferably recycled for further use in the process. Other suitable units for carrying out the process of the invention include the fluidized type process in which the hydrocarbons and catalysts are maintained in a state of turbulence in a reaction zone, the compact moving bed type operation 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 will serve to illustrate the process and advantages of the present invention.

Example I

Precipitated alumina was prepared by mixing aluminum nitrate solution with aqueous ammonia solution at a temperature of 84° F. to yield a precipitate of aluminum hydroxide. The resulting slurry was aged for 2 hours at room temperature and the precipitate was then filtered. The wet cake was washed with water containing 0.03 percent by weight of ammonia. Five 10-gallon washes were used. The wet cake was recovered after the fifth wash.

The wet alumina cake was dried in air at 200° F. for about 24 hours. The resulting dried cake was granulated and calcined in dry air for 2 hours at 950° F. The calcined granules were ground to pass 100 mesh (Tyler). The resulting powder in the amount of 154.3 grams was evacuated to a pressure of 4 millimeters of mercury. The vacuum was broken by the introduction of gaseous carbon dioxide and the pressure was raised to 2 pounds p.s.i.g. Contact between the powder and gaseous CO_2 was maintained for 30 minutes. Thereafter, while the alumina powder was in contact with carbon dioxide, 216 cc. of chloroplatinic acid containing 0.926 gram of platinum was added and mixed with the alumina to a uniform consistency. The impregnated alumina was allowed to soak for 24 hours at room temperature. Thereafter, the alumina was dried in air at 200° F. for 14 hours. The dried cake was ground to pass 100 mesh (Tyler). The resulting powder was pelleted to tablets having a diameter of ⅛" and a thickness of 1/16". The tablets were then calcined in dry air for 2 hours at 950° F. and thereafter cooled to room temperature in dry air.

The catalyst so prepared had the following properties:

Platinum, percent wt.	0.61
Chloride, percent wt.	0.54
Density, g./cc.	0.73
Surface area, $m.^2/g.$	282

Example II

A catalyst was prepared identical with that of Example I with the exception that the alumina, after evacuation, was not subjected to pretreatment with gaseous carbon dioxide but was contacted directly with the chloroplatinic acid solution.

The catalyst so prepared had the following properties:

Platinum, percent wt.	0.61
Chloride, percent wt.	0.52
Density, g./cc.	0.66
Surface area, $m.^2/g.$	307

Example III

A wet alumina cake prepared as described in Example I was dried to a moisture content of approximately 50 percent by weight and thereafter extruded to 1/16" diameter pellets. The resulting pellets were dried at 200° F. in air and then calcined in dry air for 2 hours at 950° F. The calcined pellets, in the amount of 100 grams, were evacuated to a pressure of 4 millimeters of mercury. The vacuum was broken by the introduction of gaseous carbon dioxide and the pressure was raised to 2 p.s.i.g. Contact between the pellets and carbon dioxide was maintained for 30 minutes. The pellets were thereafter evacuated to a pressure of 25 millimeters of mercury. Chloroplatinic acid solution in the amount of 72 cc. and containing 4.87 grams of platinum per liter was brought into contact with the evacuated pellets. The resulting impregnated alumina pellets were maintained in contact with the chloroplatinic acid solution for 24 hours at room temperature. The resulting pellets were then dried in air for about 2 hours at 200° F. The resulting dried catalyst was heated in dry air up to 950° F. and held at this temperature for 2 hours. The calcined catalyst was then purged 5 minutes with nitrogen and then contacted with hydrogen for 2 hours at 950° F. The catalyst so treated was then cooled in nitrogen to room temperature.

The finished catalyst had the following properties:

Platinum, percent wt.	0.34
Chloride, percent wt.	0.36
Density, g./cc.	0.63
Surface area, $m.^2/g.$	246

Example IV

A wet alumina cake prepared as in Example I was dried in air at 200° F. for about 24 hours. The dried cake was then granulated and calcined in dry air at 950° F. for 2 hours. The resulting calcined alumina was ground to pass 100 mesh (Tyler). The ground powder (413 grams) was mixed with 433 cc. of chloroplatinic acid solution containing 3.23 grams of platinum per liter. The resulting impregnated powder was dried in air at 200° F. and then sized to 6–20 mesh (Tyler). The sized catalyst was heated in nitrogen to 450° F. and then treated for 2 hours with hydrogen at 450° F., and finally heated to 950° F. and held at this temperature for 2 hours. The resulting catalyst was cooled to 100° F. in nitrogen.

The finished catalyst had the following properties:

Platinum, percent wt.	0.34
Chloride, percent wt.	0.35
Density, g./cc.	0.55
Surface area, $m.^2/g.$	208

Each of the above catalysts was tested for reforming activity by determining the dehydrogenation activity index and the acid activity index thereof.

The data in the following table illustrate the advantage of using carbon dioxide gas for preparing a platinum-alumina catalyst. Catalysts of Examples I and III were made by the method of the invention employing a gaseous carbon dioxide pretreatment of the alumina prior to impregnation. Catalysts of Examples II and IV were not subjected to pretreatment with gaseous carbon dioxide.

Catalyst Example No.	I	II	III	IV
Platinum, Percent Wt.	0.6	0.6	0.35	0.35
CO_2 Pretreatment	Yes	No	Yes	No
Dehydrogenation Activity [1]	1,030	------	800	270
Acid Activity/cc.[2]	0.9	0.3	0.6	------
Block Temp. for 98 Octane (+3 ml. TEL) °F.[3]	921	------	929	946

[1] This test measures the dehydrogenation activity of platinum in a catalyst. The test conditions are: 5,000 LHSV; 350 p.s.i.g.; 4/1 H_2/HC; 750° F. temperature; cyclohexane charge stock. The benzene yield is a measure of dehydrogenation, activity which is reported as moles benzene/second/g. catalyst, multiplied by (10)^6. The result of this test is an indication of platinum distribution.

[2] A correlation has been found between the acid activity per cc. of Pt-Al_2O_3 catalysts and the block temperature required to produce 98 CFRR +3 ml. TEL reformate at the following test conditions: August naphtha—charge; 500 p.s.i.g.; 2 LHSV; 10 H_2/HC. The acid activity test measures the rate of gas formation, when passing cumene over the catalyst at 800° F.; 175 LHSV; 1 Atmos.; 20–40 mesh catalyst size.

[3] The conditions for the reforming test are as shown under note (2). The CFRR+3 ml. TEL octane rating is determined on the reformate.

A comparison of the activity data in the foregoing table shows that the catalysts made employing a pretreatment of the alumina with gaseous carbon dioxide are more active than those which were made without having undergone such pretreatment. It is particularly to be noted that the reforming temperature for 98 octane reformate was 17° F. lower for catalyst III which had been prepared utilizing a carbon dioxide pretreatment than for catalyst IV which had not undergone such pretreatment. It is further to be noted that the dehydrogenation activity at the 0.35 weight percent platinum level was almost three times higher for the carbon dioxide-treated catalyst III as compared with catalyst IV which had not undergone pretreatment with carbon dioxide.

I claim:

1. A method of manufacturing a catalyst, which comprises pretreating porous alumina to replace substantially all of the air in the pores thereof with gaseous carbon dioxide and thereafter, while maintaining the treated alumina out of contact with air, effecting impregnation thereof with a solution of chloroplatinic acid in an amount to form a final catalyst containing from about 0.05% to about 5% by weight of platinum and calcining the resulting composite at a temperature of from about 500° F. to about 1000° F.

2. A method of manufacturing a catalyst, which comprises substantially saturating porous alumina with gaseous carbon dioxide and thereafter impregnating the alumina maintained in a gaseous carbon dioxide atmosphere with a solution of a halo-platinum acid in an amount to form a final catalyst containing from about 0.1% to about 2% by weight of platinum and from about 0.1% to about 8% by weight of halogen and calcining the thus impregnated alumina.

3. A method of manufacturing a catalyst, which comprises pretreating a porous alumina support to replace substantially all of the air in the pores thereof with gaseous carbon dioxide and thereafter, while maintaining the treated alumina out of contact with air, impregnating the same with a solution of a platinum compound and calcining the thus impregnated support.

4. A method of manufacturing a catalyst, which comprises substantially saturating a porous alumina support with gaseous carbon dioxide and thereafter, while maintaining the treated alumina out of contact with air, impregnating with a solution of a platinum compound in an amount to form a final catalyst containing from about 0.05% to about 5% by weight of platinum and calcining the resulting composite.

5. 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, substantially saturating the resulting halogen-containing alumina with gaseous carbon dioxide, impregnating the alumina so treated, prior to contact thereof with air, with a solution of a platinum compound in an amount to form a final catalyst containing from about 0.05% to about 5% by weight of platinum and calcining the resultant mixture.

6. In the manufacture of a platinum-alumina catalyst wherein a halogen is combined with porous 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 and the resulting mixture calcined to form a final catalyst containing from about 0.05 to about 5% by weight of platinum, the improvement which comprises substantially saturating the halogen-containing porous alumina with gaseous carbon dioxide, prior to contact thereof with said platinum-containing solution.

7. A method of manufacturing a catalyst, which comprises evacuating a porous alumina support, treating the evacuated alumina with gaseous carbon dioxide to effect substantial saturation thereof and thereafter, while maintaining the treated alumina out of contact with air, impregnating the same with a solution of a platinum compound and calcining the thus impregnated alumina.

8. A catalyst produced by the method of claim 4.

9. A catalyst produced by the method of claim 5.

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