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CATALYTIC REFORMING PROCESS

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This invention relates to a reforming process and more particularly to a reforming process using catalysts comprising alumina, platinum and combined halogen.

The use of an alumina-platinum-combined halogen catalyst has recently been developed in the process now known in the art as "platforming" for the treatment of a low antiknock gasoline in order to improve its antiknock properties. In this process a gasoline fraction, which generally will comprise a saturated gasoline such as straight run gasoline, natural gasoline, etc. but which also may contain varying amounts of unsaturated gasoline such as thermally cracked gasoline, etc., is subjected to contact with the catalyst at reforming conditions in order to improve the antiknock characteristic of the gasoline. The gasoline may comprise a full boiling range gasoline fraction having an initial boiling point of from about 50° to about 100° F. and an end boiling point of from about 375° to about 425° F. or it may be a selected fraction which usually will be a higher boiling fraction, commonly referred to as naphtha, and generally having an initial boiling point of from about 150° to about 250° F. and an end boiling point of from about 350° to about 425° F.

The platforming catalyst comprises alumina, platinum in an amount of from about 0.01% to about 1% by weight and from about 0.1 to about 8% by weight of halogen. The platinum and halogen are combined with each other and/or with the alumina. The preferred catalyst comprises alumina, platinum in the amount hereinbefore set forth and combined fluorine in an amount of from about 0.1% to about 3% by weight. In still another preferred embodiment the catalyst also contains combined chlorine, the total amount of halogen being within the range of from about 0.1% to about 3% by weight.

It has now been found that unexpected improved results are obtained when the catalyst is utilized as small size particles which will measure not more than about $\frac{3}{32}$'' across the widest portion. It has been found that, with this particular platforming catalyst, not only is a more active catalyst obtained, but also the unexpected advantages of a longer catalyst life and of a decreased carbon deposit formation. These results are contrary to expectations because normally, with other catalysts, it has been found that a more active catalyst results in a shorter life and increased carbon formation.

These unexpected advantages are peculiar to the platforming process because of the specific reactions occurring therein. These reactions include primarily the dehydrogenation of naphthenic hydrocarbons to aromatics, the selective cracking of long chain aliphatic hydrocarbons to produce smaller size hydrocarbons, and the isomerization of the straight chain or slightly branched aliphatic hydrocarbons. In addition, aliphatic hydrocarbons are dehydrogenated and cyclicized to aromatics, hydrogen transfer reactions occur, etc. The dehydrogenation reaction is highly endothermic and, therefore, applicant believes that the following explanation will account, at least in part, for the unexpected improved results obtained by the use of smaller size particles. However, it is understood that the present invention is not limited to this explanation. The dehydrogenation reaction occurs very readily and this reaction, being highly endothermic, results in a temperature gradient throughout the catalyst particle. This, in turn, results in an uneven carbon distribution, as well as in a low production of aromatics in the interior of the catalyst particle. Thus, with a larger size pill, this is believed to result in interference with the diffusion of the reactants into the interior of the catalyst particle, which interference occurs at very low carbon levels and causes a rapid decline in catalyst activity. However, by utilizing smaller size particles, there is very little interference with diffusion of the reactants through the catalyst because what would be the interior of a large size pill is now exposed to the reactants when using a smaller size pill.

The shift in temperature relationship occurring during the dehydrogenation reaction in turn affects the balance between aromatization and selective cracking required for an optimum yield-octane relationship. The selective cracking and other reactions are only slightly exothermic and, therefore, this balance is upset by large differences in temperature between the outside and the interior of the catalyst particle. As will be shown in the examples, the average temperature of the catalyst bed is lower when using the smaller size particles and this indicates that the reaction is effected at an overall lower temperature with the smaller size particles. On the other hand, with the larger size particles, the temperature at the outside of the catalyst particle is higher and this, therefore, results in a higher average catalyst temperature for effecting the same reaction.

In one embodiment the present invention relates to a process for reforming a gasoline fraction which comprises subjecting said fraction to contact with a catalyst comprising alumina, platinum and combined halogen, said catalyst being of a particle size not greater than $\frac{3}{32}$'' across the widest portion of the particle.

In a specific embodiment the present invention relates to a process for reforming of a straight run gasoline which comprises subjecting said gasoline to contact at reforming conditions with a catalyst comprising alumina, platinum in an amount of from about 0.01% to about 1% by weight and combined fluorine in an amount of from about 0.1% to about 3% by weight, said catalyst being further characterized in that the particle size thereof is from about $\frac{1}{32}$'' to about $\frac{3}{32}$'' across the widest portion thereof.

The platforming catalyst may be manufactured in any suitable manner. In view of the fact that the platinum and halogen are utilized in so small amounts, it is essential that the catalyst be free from impurities in amounts which may offset or mask the effect of the small amounts of activating components. In view of the fact that the alumina comprises over 90% of the catalyst, a particularly preferred method of eliminating impurities is to purify the aluminum salt used as a source of the alumina or to purify the alumina prior to compositing the other components therewith. Although any suitable salt of aluminum may be utilized in the preparation of the alumina, including aluminum acetate, aluminum sulfate, aluminum nitrate, etc., a particularly preferred salt is aluminum chloride. The alumina is readily prepared by reacting aluminum chloride with a suitable basic reagent, such as ammonium hydroxide, ammonium carbonate, etc. in an amount to form aluminum hydroxide which upon drying is converted to alumina and, in the interest of simplicity, the aluminum hydroxide is referred to as alumina in the present specification and claims in order that the percentages are based on the alumina free of combined water.

The resultant alumina will be a more or less gelatinous mass and then may be washed and filtered to remove soluble impurities. In order to avoid the introduction of other impurities, it is preferred that the water used for this washing be purified so that no undesirable impurities will be introduced from this source. It has been found that the washing treatment is improved when the wash water contains a small amount of ammonium hydroxide. The severity of washing will depend upon the particular catalyst desired. For example, when a chloride free catalyst is desired, the washing will be more severe to insure removal of substantially all chlorine. On the other hand, when a portion of the chlorine is desired in the final catalyst, the washing will be controlled to leave the desired amount of chlorine in the catalyst. However, as a general rule, when a specific amount of chlorine is desired in the catalyst, it generally is desirable to thoroughly wash the alumina and then add the desired chlorine in a subsequent step because better control of the concentration of chlorine is obtained in this manner.

In a preferred embodiment of the invention fluorine, preferably as hydrogen fluoride, is added to the final wash water, the amount of fluorine will be controlled to give the desired fluorine concentration and the water used in the final step will not contain ammonium compounds. The alumina containing halogen is then partially dried at a temperature of from about 200° to about 500° F. for a period of from about 2 to 24 hours or more to form a cake. In one embodiment the cake may be ground to a particle size of not greater than $\frac{3}{32}$'' across the widest portion and then platinum is introduced into the composite of alumina and halogen. In another embodiment, the partially dried particles of alumina and combined halogen may be calcined at a temperature of from about 800° to about 1400° F. for about 2 to 12 hours or more and then platinum may be introduced into the composite. In still another method the platinum may be added to the slurry of alumina before drying and either before or after the halogen is added thereto, and the resultant composite may then be dried, ground and calcined or dried, calcined and ground. In the case where the platinum is introduced in the catalyst, the calcination temperature should not be above about 1000° F. and preferably is within the range of from about 600° to about 1000° F.

When the platinum is to be added to the previously dried and calcined alumina-halogen composite, it preferably is added as a solution of a suitable platinum compound which also contains a small amount of ammonia as it has been found that the ammoniacal solution improves impregnation. When the platinum is to be added to the alumina before drying, the platinum is preferably added in a suitable solution containing hydrogen fluoride which has been found to assist in the impregnation.

Any suitable platinum compound may be used in preparing the catalyst and preferably comprises chloroplatinic acid because of its ready availability. Other suitable platinum solutions include ammonium platinum chloride, trimethyl benzyl ammonium platinum chloride, tetramino platino chloride, ammonium platino nitrite, etc. The platinum solution used for the impregnation should not contain undesirable impurities in order not to introduce the impurities into the catalyst from this source.

When the platinum is added to the alumina before drying, the composite of alumina, combined halogen and platinum is dried and calcined at temperatures hereinbefore set forth and the catalyst is then ground into particles of a size not greater than $\frac{3}{32}$''. When the platinum is added to the dried and calcined alumina-halogen composite, the desired particles size is preferably obtained by grinding or otherwise forming the alumina-halogen composite into particles of a size not greater than $\frac{3}{32}$'' prior to the addition of the platinum.

It is understood that the catalyst may be formed into the desired small size particles in any suitable manner. For example, the catalyst may be formed into particles of uneven size and shape by grinding or it may be formed into pills of uniform size and shape either in a pelleting or extrusion operation. In another embodiment, the catalyst may be formed into spheres of the desired diameter in any suitable manner.

As hereinbefore set forth, it is an essential feature of the present invention that the catalyst be utilized in the form of particles of less than $\frac{3}{32}$'' in size across the widest portion. The lower limits of the size of the particles will be determined by practical considerations. For example, the smaller the size particles, the greater will be the pressure drop through the reaction chamber. As a general rule, the smallest size particles to be employed will be about $\frac{1}{32}$'', although it is understood that smaller size particles may be employed when desired.

The catalyst as prepared in the above manner will be utilized in the reforming of a gasoline fraction at a temperature of from about 600° to about 1000° F., a pressure of from about 50 to about 1000 pounds per square inch and a weight hourly space velocity of from about 0.5 to 10. The weight hourly space velocity is defined as the weight of oil per hour per weight of hydrocarbons in the reaction zone. The reforming operation is effected in the presence of hydrogen which may be recycled within the process in order to eliminate the necessity of introducing hydrogen from an extraneous source except at the start of the process.

As hereinbefore set forth, the platforming process includes dehydrogenation, selective cracking and isomerization reactions. In another embodiment of the invention the dehydrogenation reaction may be effected in one zone, and the other reactions may be effected in successive zone or zones. For the reasons hereinbefore set forth, it may be desirable to utilize the smaller size particles in the first zone to accomplish a major portion of the aromatization reaction and to utilize larger size particles, which may range from ⅛" to ¼" or more in size, in the other zone or zones to effect the remaining portion of the aromatization and substantially all of the selective cracking and isomerization. In still another embodiment of the invention, separate beds of catalyst may be utilized in a single chamber, the first bed comprising the smaller size particles and the remaining bed or beds comprising the larger size particles.

The reforming process 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 is preferably recycled for further use within the process. Other suitable units in which the process may be effected include the fluidized type process in which the hydrocarbons and catalysts are maintained in a state of turbulence under hindered settling conditions in a reaction zone, the compact moving bed type in which the catalyst and hydrocarbons are passed either concurrently or countercurrently to each other, and the suspensoid type of operation in which the catalyst is carried into a reaction zone as a slurry in the gasoline.

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

Example I

A platforming catalyst was prepared by reacting aluminum chloride hexahydrate with ammonium hydroxide to precipitate alumina. The alumina was washed with water containing ammonium hydroxide and filtered a number of times. The filter cake was then slurried with water and an aqueous hydrogen fluoride solution was commingled therewith, after which the slurry was filtered. The filter cake was dried at a temperature of about 350° F., ground and then calcined at a temperature of about 1100° F. Sterotex was added as a lubricant to the ground calcined particles which were then formed into cylindrical pills of ⅛" x ⅛" in size in a conventional pelleting machine. The pills were impregnated with an ammoniacal solution of chloroplatinic acid and then were dried and calcined at a temperature of about 900° C. in the presence of air.

The catalyst pills as prepared in the above manner were split into two portions. One portion was used as such and the other portion was ground into particles of 12–30 mesh. This corresponds to particle sizes of smaller than 1/16 of an inch. The separate portions were used in the separate reforming of a Mid-Continent naphtha at a furnace temperature of 932° F., a pressure of 500 pounds per square inch gauge, a space velocity of 12, and a hydrogen : hydrocarbon ratio of 3:1. Each reforming operation was carried out for 22 hours and the extent of aromatization was measured hourly throughout the run, along with octane numbers of composite samples. The results of these runs are shown in the following table.

TABLE I

	Run No. 1	Run No. 2
Form of catalyst	⅛" x ⅛" pills.	12–30 mesh granules.
Average catalyst temperature, ° F	896	869.
Product:		
Dispersion after ½ hour	107.1	110.7.
Dispersion after 2 hours	106.5	110.2.
Dispersion after 8 hours	105.5	109.6.
Dispersion after 16 hours	104.5	109.2.
Dispersion after 22 hours	103.8	108.9.
Net change in dispersion	3.3	1.8.
A. S. T. M. Research Octane Number, clear:		
at start	56.1	60.2.
at middle	57.2	60.3.
at end	53.5	60.4.
Carbon	1.10	1.02.

It will be noted from the data in the above table that the dispersion was lower at the start with the ⅛" catalyst pills and also that the change in dispersion was greater with the ⅛" catalyst pills as compared to the 12–30 mesh granules. The higher dispersion indicates a higher aromatic content. This means that the ⅛" pills, not only produced less aromatics at the start of the operation, but also decreased in activity to produce aromatics at a faster rate than the 12–30 mesh granules. This lower initial activity and greater decline is also indicated in the octane numbers as shown in the above table. Still further, it will be noted that the amount of carbon with the ⅛" pills is greater than the amount of carbon with the 12–30 mesh granules.

Of particular interest is also the fact that, with the same furnace temperature of 932° F. in both cases, the average catalyst temperature of the ⅛" pills was 27° F. higher than the catalyst temperature of the 12–30 mesh granules. This definitely shows that the interior of the ⅛" pills is at a much lower temperature level than the outside of the pill.

As hereinbefore set forth, this higher initial activity coupled with longer life and less carbon is unexpected and is due to the peculiar reactions occurring in the platforming process.

Example II

Another batch of platforming catalyst was prepared in substantially the same manner. One portion of the catalyst was pilled to 1/16" size and the other portion was pilled to ⅛" size. The results of the reforming of a Mid-Continent naphtha at a furnace temperature of 977° F., a pressure of 300 pounds per square inch gauge, a space velocity of 12 and a hydrogen:hydrocarbon ratio of 1.5:1 are shown in the following table.

TABLE II

	Run No. 3	Run No. 4
Form of catalyst	$\frac{1}{8}$'' pills	$\frac{1}{16}$'' pills.
Dispersion data:		
First 3 hours	111.7	113.7.
Final 2 hours	106.9	110.0.
Decrease	4.8	3.7.
Weight percent of aromatics:		
First 3 hours	53.6	56.0.
Final 2 hours	47.3	51.2.
Decrease	6.3	4.8.
Carbon on catalyst, weight percent	4.98	3.01.

Here again it will be noted that the smaller size particles produced a higher yield of aromatics, a smaller decline in aromatic production and lower carbon formation as compared to the larger size pills.

Example III

In order to obtain a more direct comparison based upon the same initial conversion level (average aromatic production during the first 3 hours), another run was made with the $\frac{1}{8}$'' pills at a higher temperature. The temperature selected was 988° F. and it will be noted, from the data in the following table, that the aromatics produced at the higher temperature with the $\frac{1}{8}$'' pills amounted to 55.3% as compared to an aromatic production of 56% when using the $\frac{1}{16}$'' pills at the lower temperature of 977° F. These data in the following table, for ease in comparison, repeats the data of run No. 4 which also is reported in Table No. II.

TABLE III

	Run No. 5	Run No. 4
Form of catalyst	$\frac{1}{8}$'' pills	$\frac{1}{16}$'' pills.
Dispersion data:		
First 3 hours	113.1	113.7.
Final 2 hours	104.1	110.0.
Decrease	9.0	3.7.
Weight percent of aromatics:		
First 3 hours	55.3	56.0.
Final 2 hours	43.6	51.2.
Decrease	11.7	4.8.
Carbon on catalyst, weight percent	7.25	3.01.

It will be noted from the above table that the decrease in dispersion, decrease in aromatic production and increase in carbon is more than double for the run utilizing $\frac{1}{8}$'' pills as compared to the run utilizing $\frac{1}{16}$'' pills.

I claim as my invention:

1. A process for the reforming of a gasoline fraction which comprises subjecting said gasoline fraction to contact at reforming conditions with at least two successive beds of catalyst comprising alumina, platinum and combined halogen, the catalyst in the bed with which said fraction is first contacted being of a particle size not greater than $\frac{3}{32}$'' and the catalyst in a subsequent bed being of a particle size greater than $\frac{3}{32}$''.

2. A process for the reforming of a gasoline fraction which comprises subjecting said gasoline fraction to contact at reforming conditions with successive beds of a catalyst comprising alumina, from about 0.01% to about 1% by weight of platinum and from about 0.1% to about 3% by weight of combined fluorine, the catalyst in the bed with which said fraction is first contacted being of a particle size not greater than $\frac{3}{32}$'' and the catalyst in a subsequent bed of the series being of a particle size greater than $\frac{3}{32}$''.

3. In the reforming of a gasoline fraction by contact thereof at reforming conditions with a catalyst comprising alumina, platinum and combined halogen, the improvement which comprises initially passing the gasoline fraction through a bed of said catalyst of a particle size not greater than $\frac{3}{32}$'' and thereafter through a second bed of said catalyst of a particle size greater than $\frac{3}{32}$''.

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