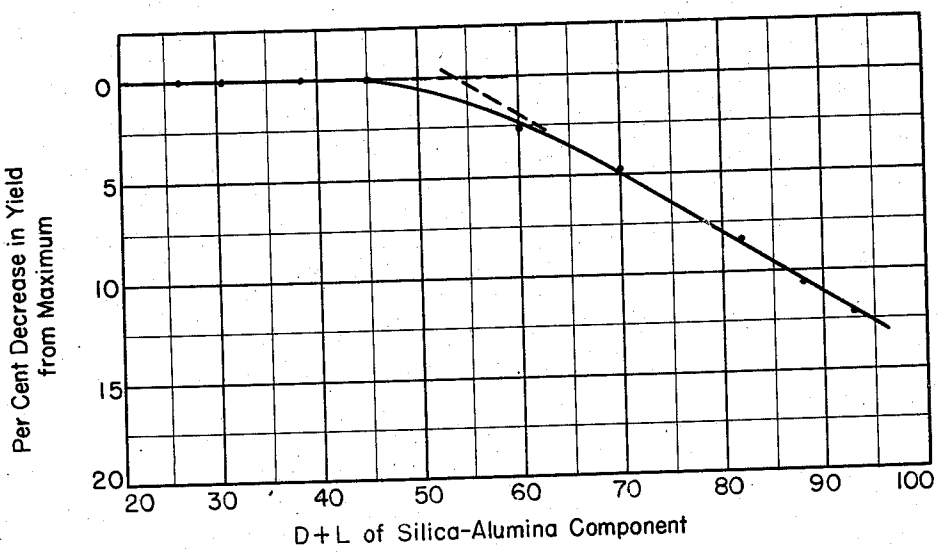
April 28, 1959 J. E. CONNOR, JR., ET AL 2,884,374

PLATINUM-CONTAINING CATALYSTS AND METHOD OF PREPARATION THEREOF

Filed Oct. 22, 1954 2 Sheets-Sheet 1

Figure 1.



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PLATINUM-CONTAINING CATALYSTS AND METHOD OF PREPARATION THEREOF

Filed Oct. 22, 1954 2 Sheets-Sheet 2

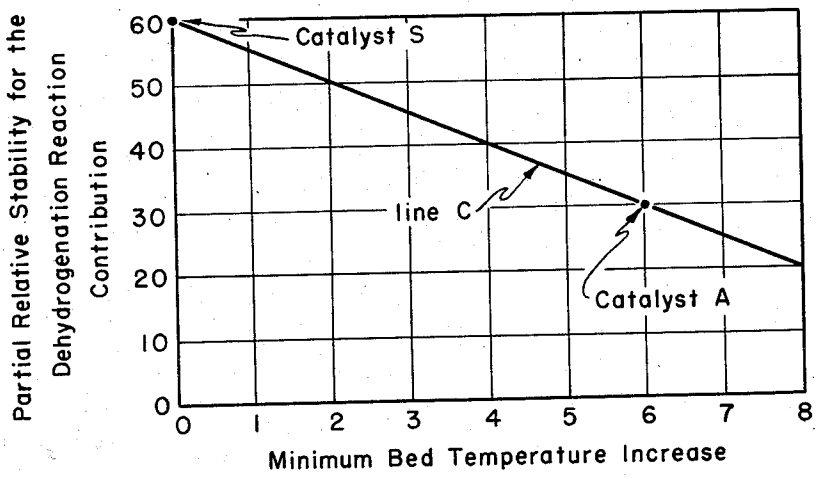


FIG. 2

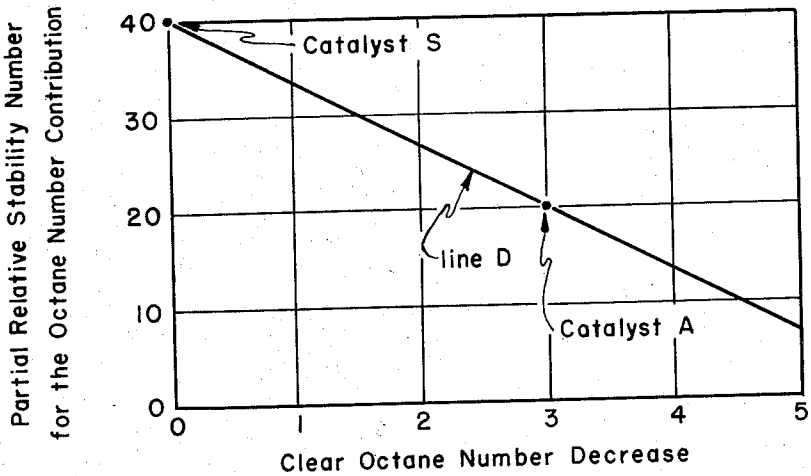


FIG. 3

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2,884,374

PLATINUM-CONTAINING CATALYSTS AND METHOD OF PREPARATION THEREOF

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Application October 22, 1954, Serial No. 463,851

7 Claims. (Cl. 208—138)

This invention relates to platinum-containing catalysts and to their method of preparation and use, and more particularly to platinum-containing catalysts having a high stability prepared from a specific complex compound of platinum and to the use of such catalysts in reforming processes.

In the past few years the octane requirements of automotive engines have been steadily increased. Furthermore, the percentage of various makes of cars requiring premium fuels of exceptionally high octane in order to obtain the performance built into them by the manufacturers has been increased. For example, in the year 1950 a fuel of 90 octane number was sufficient to satisfy the requirements of any engine. By 1954, fuels of 94.5 to 95 octane were necessary for efficient operation of all engines and the number of units requiring such fuels had increased their proportion and numbered several million, thus not only was an extremely high octane fuel required but much larger volumes were likewise required. In addition, it has been predicted by many automotive and petroleum experts that by 1958 fuels of 98 octane number will be required in even greater quantities since an even higher percentage of engines will require such fuels.

This problem is aggravated by the fact that in order to produce the necessary quantities of fuels it is necessary that many sources of crude petroleum be used which are not particularly suited for production of these extremely high octane gasolines. For many years petroleum refiners found the necessary quantities of motor fuels of the required octane level could be produced by combining the products of catalytic cracking, thermal cracking and thermal reforming with straight run naphthas. However, a number of years ago it was found necessary to up-grade in octane the thermal and straight run products. In order to accomplish this, refiners turned to catalytic reforming.

Straight run and thermally cracked gasoline fractions are composed of straight chain, slightly branched chain, cyclic paraffins and olefins, all of which have relatively low octane values, together with only minor amounts of aromatics.

Several reactions are possible whereby the octane value of straight run and thermally cracked gasoline fractions may be increased. These reactions include the isomerization of straight chain and slightly branched chain hydrocarbons to more highly branched chain compounds, the isomerization of the cyclic saturated compounds (naphthenes) to six carbon ring structures suitable for dehydrogenation to the corresponding aromatics, the dehydrogenation of six carbon ring naphthenes to the corresponding aromatics, the conversion of paraffins to aromatics by dehydrocyclization, and the selective cracking of high molecular weight hydrocarbons to compounds of lower molecular weight in the gasoline boiling range.

Although many compositions have been proposed as being useful in promoting one or more of the above reactions, only certain platinum impregnated acidic metal oxide component catalysts are known to be capable of successfully promoting all of the desired reactions in a

ratio which will give the greatest octane improvement with the lowest loss in yield. One example of such a catalyst contains silica combined with alumina as the acidic metal oxide component. Other acidic metal oxide components which may be impregnated with platinum for use in this invention include: silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, silica-thoria, silica-alumina-thoria, alumina-thoria, and similar oxide combinations. These metal oxide components are characterized by having exchangeable hydrogen ions in their structure. Their preparation and properties have been published widely both in patents and in technical literature. Therefore, for purposes of brevity, this information will not be reiterated here. Likewise, the proportions of the various individual oxides which can be combined to produce the acidic metal oxide component may vary over relatively wide ranges as has been set forth in the prior patent and literature art.

It is necessary when using these catalysts in a reforming operation, however, to have present rather large amounts of hydrogen which functions to maintain the catalyst in a clean condition, free of coke and carbonaceous deposits which would substantially deactivate the catalyst if allowed to accumulate. Since there is a net production of hydrogen in the over-all reforming reaction, there is no serious problem with respect to hydrogen supply. To make the hydrogen effective, super-atmospheric pressures must be used or, in other words, the hydrogen partial pressure must exceed one atmosphere.

The dehydrogenation reaction is one of the most rapid of the reforming reactions and, therefore, under most operating conditions, equilibrium can be readily reached between the naphthenes and the aromatics. Since, however, the volume of the products exceeds the volume of the reactants, the reaction is of course affected by pressure in the reverse direction—that is, the formation of aromatics is decreased as the pressure is raised at a constant reaction temperature. In addition, it is well-known that at a constant pressure, as the reaction temperature is increased, the equilibrium shifts in the direction of higher aromatic production. It follows, therefore, that since it is highly desirable to have the equilibrium as far as possible in the direction of maximum production of aromatics and, since super-atmospheric pressures must be used, higher temperatures must also be employed.

To summarize the foregoing: (*a*) hydrogen at super-atmospheric pressures is necessary to maintain the reforming catalyst in a clean condition, (*b*) dehydrogenation of naphthenes to aromatics produces hydrogen and in addition furnishes an important increment of octane improvement, (*c*) equilibrium considerations require the use of elevated temperatures to produce the maximum quantities of aromatics and hydrogen at the superatmospheric pressures, (*d*) isomerization reactions must be promoted to a maximum extent within the same range of conditions where maximum aromatic formation is realized, and (*e*) cracking must be controlled to prevent formation of hydrocarbons boiling below the gasoline range. When all five of these requirements are met simultaneously in a reforming process, that is when all of the desired reactions are in proper ratio one to the other, there results the optimum yield-octane relationship for the process.

Although several catalysts have been described in the prior art wherein one of the abovementioned acidic metal oxide components has been impregnated with platinum, these catalysts have all been subject to a common disadvantage, namely, that they cannot be used to produce 95 or higher CFRR octane number fuels commercially in plant scale operations. Where it is said that an engine requires a 95 CFRR octane number gasoline, it is of course apparent that this level may be reached by adding

tetraethyl lead to a base stock in amounts up to 3 cc. per gallon. Thus, the clear (no tetraethyl lead) CFRR octane number of the catalytically reformed product may range between 82 and 84 CFRR octane level and the 95 level reached by addition of 3 cc. of tetraethyl lead per gallon. Obviously since 3 cc. of tetraethyl lead per gallon is the maximum amount for automotive fuel permitted by law, it is desirable to produce a base stock having a clear CFRR octane number of about 85 to 86 such that a lower amount, of the order of 2.5 cc. tetraethyl lead per gallon is required to produce the 95 octane number motor fuel. Moreover, since the incremental increase in octane number which can be obtained by addition of tetraethyl lead decreases as the octane level increases, it is necessary, for example, to have base stocks of almost 90 CFRR clear octane number to produce a 98 CFRR octane number by addition of 3 cc. tetraethyl lead per gallon. Furthermore, very recently it has been found that large amounts of tetraethyl lead sometimes produce undesirable engine performance because of such phenomena as surface ignition. Consequently, in order to produce the required 95 and higher octane level fuels the catalytically reformed product must have a CFRR clear octane number of from about 86 to 90.

In order to produce the 95 octane number fuels and higher with these catalysts under continuous operation it has been found necessary to use high initial reaction temperatures to reach the 86 to 90 clear octane level. With these high temperature levels, the activity of these catalysts declines rapidly with use and in order to maintain the required octane level, the reaction temperature must be raised still further which results in an even more rapid decline in activity. The net result of these operations is that the catalysts have extremely short lives, making them economically unfeasible for use in commercial operations.

This decline in activity is manifested by a decline in ability of the catalyst to promote the dehydrogenation reaction, that is, the conversion of naphthenes to aromatics, and in the ability of the catalyst to promote the isomerization reaction at the temperature levels required for optimum dehydrogenation. In addition, as the dehydrogenation ability of the catalyst declines, its ability to control the hydrocracking reaction likewise disappears with the result that uncontrolled cracking occurs and yield of gasoline boiling range product decreases. The measure of a catalyst's resistance to this decline in activity will herein after be referred to as its stability.

Since the aforementioned catalysts suffered universally from the same disadvantage, namely, lack of stability at severe reforming conditions, it is reasonable to assume that this characteristic was due to an inherent property of such catalysts, to a common defect introduced in their preparation, or to a combination of these factors.

It is an object of the instant invention to provide a catalytic reforming process which will produce high octane gasoline at high yields employing a catalyst which is stable under the required reforming conditions.

It is an additional object of this invention to provide a catalyst which will promote dehydrogenation of hydrocarbons and isomerization of hydrocarbons and simultaneously control the hydrocracking reaction under all reforming conditions.

It is a further object of this invention to provide a reforming catalyst which is stable under severe reforming conditions.

Additional objects will be apparent from the following description.

In accordance with the present invention an acidic metal oxide component whose activity for the cracking of hydrocarbons has been altered is treated with an aqueous solution of platinous tetramminohydroxide to impregnate platinum thereon in the form of the complex cation and thereafter the treated component is dried and treated

at elevated temperatures to convert the platinum compounds to metallic platinum.

The acidic metal oxide components which are impregnated with the platinum complex include silica and at least one metal oxide from the group consisting of alumina, zirconia, magnesia, and thoria. In general, an acidic metal oxide component having a catalytic cracking activity in the range between 20 and 65 distillate-plus-loss as measured according to the method of Birkhimer, Macuga, and Leum, in "A Bench Scale Test Method for Evaluating Cracking Catalysts," Proceedings of the American Petroleum Institute, Division of Refining, volume 27 (III), page 90 (1947), is required. Various other methods of measuring the catalytic cracking activity of such acidic metal oxide components have been described in the literature. A summary of the most widely used methods, including the Birkhimer et al. method, appears in "Catalytic Cracking Techniques in Review," by Marshall Sittig, Petroleum Refiner, pages 274–275, volume 31, No. 9 1952). The Birkhimer et al. reference mentioned above gives a comparison of several methods, therefore, if it is desired to compare the activity as described in terms of the Birkhimer et al. "D+L" with other activity measurements, it is only necessary to refer to the comparisons mentioned in such review.

According to the Birkhimer et al. D+L (distillate-plus-loss) activity measurement method, it would be possible to have a theoretical maximum D+L of 100. However, in general, for a fresh silica-alumina cracking catalyst the maximum D+L will range between 90 and 95. Since the other catalytic activity measurement methods which employ a D+L measure give much lower values for a fresh silica-alumina cracking catalyst, usually of the order of 45 to 65 depending upon the particular test, it is apparent that when one specifies a D+L scale having practicable maximum activity of 90 to 95 the Birkhimer et al. test is being employed.

Various methods of altering the cracking activity of acidic metal oxide components have been disclosed in the prior art. For example, the acidic metal oxide may be treated with steam at temperatures of from 900° F. to 1400° F. at pressures ranging from atmospheric to several hundred pounds per square inch for a period of time sufficient to provide the desired degree of alteration. Other methods may be used for modifying the catalytic activity of such components; for example, by varying the amount of the metal oxide combined with the silica or by incorporating a chemically combined alkali metal in the component.

As has been pointed out, the method of preparing acidic metal oxide components by combining silica with various metal oxides are well known. A particularly desirable method of preparing a silica-alumina component involves adding sulfuric acid to commercial water glass in proportions to precipitate silica hydrogel; the silica hydrogel is washed with acidulated water to remove sodium ions, after which the hydrogel is dispersed in a sufficient amount of an aqueous solution of aluminum sulfate of suitable concentration and ammonium hydroxide is added to precipitate alumina to form a silica-alumina component containing 13 percent by weight of alumina. The silica-alumina component is then washed, dried, calcined at elevated temperatures and formed into pellets. Such a component will have a D+L of from 90 to 95 in terms of the Birkhimer et al. D+L measurement set forth above. Similar methods of preparing the other components mentioned herein may be used. Likewise, the proportions of the metal oxides may be varied in accordance with prior art teachings.

Further, in accordance with the present invention, one of the above-mentioned acidic metal oxide components having a cracking activity within the desired D+L range is contacted with a small excess of an aqueous solution of platinous tetramminohydroxide. In general, a ratio of 1.2 cc. of aqueous solution per gram of catalyst is pre-

ferred. This solution and the metal oxide component mixture is then heated to an elevated temperature, generally to about the boiling point of the solution, and is held at this temperature for a period of time which may range from about 4 hours to 24 hours. Treating at temperatures of 210° F. to 212° F. for a period of about 4 hours is in many cases sufficient, however, in some cases additional improvement of the catalyst has been found when the heating has been continued from 18 hours up to 24 hours. It has been noted also that if the temperature is increased as by heating under superatmospheric pressures, the heating time can be shortened. If necessary, distilled or deionized water should be added to the solution during the heating step to replace any water lost by evaporation. After the heating step, the spent solution is drained from the impregnated metal oxide component and the impregnated component preferably is dried to remove excess moisture. The dried impregnated carrier then is subjected to known conventional methods for decomposing or reducing the platinum complex to produce metallic platinum on the metal oxide components. Preferred methods for accomplishing the latter step include calcination with air or reduction with hydrogen at elevated temperatures.

The compound, platinous tetramminohydroxide, is believed to have the formula:

$$[Pt(NH_3)_4](OH)_2$$

The portion of the compound within the brackets is the complex platinum cation wherein the platinum has a valence of +2. It is believed that during the initial step of treating the acidic metal oxide component, the complex cation replaces hydrogen ions in the lattice structure of the metal oxide component, which hydrogen ions in turn are neutralized by the hydroxide ions of the platinous tetramminohydroxide. This belief is substantiated by the fact that the platinum concentration of the treating solution drops very rapidly to a low value which remains constant during the subsequent heating step.

It is one of the additional advantages of the instant invention that since the only by-product of the impregnation is water the solution remaining after the impregnation may be fortified with additional platinous tetramminohydroxide and used for treating an additional quantity of acidic metal oxide component. In prior art methods since there were other by-products of the impregnation step, it was necessary to recover the platinum from the spent impregnating solution before it could be used for impregnating an additional quantity of an acidic metal oxide component.

The concentration of platinous tetramminohydroxide can be adjusted according to the desired amount of platinum to be placed on the metal oxide component. It has been found experimentally that for the acidic metal oxide components above-mentioned an amount in excess of 95 percent of the platinum content of the solution is exchanged onto the base component. Therefore, if it is desired to produce a finished catalyst containing 0.45 percent platinum, approximately 0.02 molar solution of the platinous tetramminohydroxide should be used with a ratio of 1.2 cc. of solution per gram of metal oxide component.

In the preparation of the catalysts of the instant invention, the amount of platinum which is desired on the acidic metal oxide component generally ranges from about 0.1 percent to 2.5 percent, although it is of course possible to deposit higher percentages or lower percentages merely by adjusting the concentration of the solution of platinous tetramminohydroxide.

The impregnated acidic metal oxide component is preferably dried at conventional temperatures, such as those ranging between about 212° F. and 325° F., using ordinary commercial methods such as tumble drying or drying with hot air or nitrogen or similar gas. After removing the excess moisture, the impregnated metal oxide component is subjected to conventional methods for decomposing or reducing the platinum complex to produce metallic platinum on the oxide component. For example, this may be air calcination at temperatures ranging between about 600° F. and 1000° F.; preferably, however, between about 650° F. and 750° F. When hydrogen is used to reduce the platinum to the metallic state, temperatures ranging between 450° F. and 1000° F. may be used.

It has been pointed out that the aforementioned prior art commercial reforming catalysts have been found to be incapable of continuously producing commercial quantities of high octane fuel, for example, in the range of 95 octane or higher. In order to reach the required high octane levels using prior art catalyst compositions, it is necessary to initiate the reaction at an extremely high temperature level. These high temperatures in themselves are an extremely important cause of deactivation of these catalysts, and produce an extremely rapid decrease in the ability of the catalysts to promote the desired reforming reactions in the proportions required for efficient reforming at the high octane levels. Thus, after a very short period at the high initial temperature levels, the prior art catalysts were found to be no longer capable of producing a product at the required octane level obtained at such initial reaction temperature. Inasmuch as in a commercial unit the only condition which can be varied readily is temperature, this decrease in the ability of the catalyst to produce the required octane level was compensated for by raising the temperature. This adjustment, however, produced only a temporary solution since at the higher temperature the decline in the catalysts' activity was even more rapid than at the initial reaction temperature and thus progressively higher temperature levels were required with increasing frequency. It is obvious that this type operation quickly leads to a situation whereby it is impossible to obtain added octane improvement by raising the temperature, since the decline in activity of the catalyst outstrips the ability of the operator to compensate therefor. The sum total of these factors is that with the prior art catalysts operations for required high octane levels result in plant runs of a duration too short to be feasible for commercial operation.

The requirements, therefore, of a catalyst which can be used commercially for producing fuels of the required high octane levels are that it either be capable of producing the required octane level at a relatively low temperature or, in the alternative, that it be capable of maintaining its activity for long periods of time at extremely high temperature levels. The catalyst of the instant invention has been found to possess both of these requirements to an extremely high degree. Although the reasons for these unexpected and novel properties of the instant catalyst are not known, several theories may be advanced as a partial explanation therefor. When catalysts are prepared in accordance with the present invention, the platinum apparently is located in the neighborhood of the most catalytically active sites on the acidic metal oxide components, whereas with the prior art catalysts only that portion of the platinum as governed by probability considerations would be located near such active centers since such methods involved mere mechanical deposition. Moreover, it is apparent that in the preparation of the instant catalyst something more than base exchange is involved inasmuch as other platinum compounds wherein the platinum is in the cationic portion of the molecule, and therefore theoretically may be deposited on the acidic metal oxide component by base exchange, do not exhibit the properties of the instant catalyst as will be demonstrated hereinafter in the examples.

From the data in the examples which follow the accompanying drawings were constructed. In the drawings:

Figure 1 is a plot of the D+L of the silica-alumina component versus percent decrease in yield from maximum.

Figure 2 is a plot of the partial relative stability number for the dehydrogenation reaction contribution (minimum bed temperature increase) versus minimum bed temperature increase as determined in the laboratory reforming stability test.

Figure 3 is a plot of the partial relative stability number for the octane number contribution versus the clear octane number decrease as determined in the laboratory reforming stability test.

The examples which follow are provided for the purpose of illustrating the various aspects of the instant invention and to demonstrate the superiority of the catalysts of the instant invention over the catalysts of the prior art.

In order to demonstrate the importance of the D+L rating of the acidic metal oxide component and the necessity of employing an acid metal oxide component within the range of 20 to 65, the following experiments outlined in Example I were carried out.

EXAMPLE I

A number of catalysts were prepared wherein the D+L of the silica-alumina component prior to platinization was varied over a wide range. A large commercial sample of silica-alumina cracking catalyst was prepared by adding sulfuric acid to commercial water glass in an amount sufficient to precipitate silica hydrogel. The silica hydrogel was washed with acidulated water to remove sodium ions and then the hydrogel was dispersed in an amount of an aqueous solution of aluminum sulfate of suitable concentration such that when ammonium hydroxide was added to precipitate the alumina there was formed a silica-alumina composite containing approximately 13 percent by weight of alumina. The silica-alumina composite was then washed, dried, pelleted and calcined at 600° F. to 900° F. This cracking catalyst had a D+L rating of about 93, according to the above described Birkhimer et al. method. Several portions of the thus prepared silica-alumina component were then treated with steam at 1050° F. to 1250° F. and at 15 to 200 pounds per square inch for 3 to 18 hours to obtain components having the D+L ratings indicated in Table I. The different samples of the silica-alumina composites were impregnated with the platinous tetrammine complex ion in order to give between 0.5 percent–0.7 percent platinum on the finished catalyst. The catalysts were tested in a semi-plant scale unit wherein sufficient product was produced to obtain accurate yield-octane data. The feed stock to the test unit consisted of a typical East Texas distillate having the following properties.

ASTM distillate:

Overpoint	° F.	180
50 percent	° F.	255
95 percent	° F.	335
End point	° F.	380
Clear octane number (ASTM Method D908–53)		55
API gravity at 60° F		56.3

Prior to introduction into the unit the feed was preheated to various temperatures ranging between 750° F. and 940° F. in order to give a range of octane levels and yields corresponding to such octane levels. Liquid hourly space velocities of 3 and of 6 were employed at the various temperatures and sufficient recycle hydrogen was introduced with the feed to maintain a hydrogen to hydrocarbon mol ratio of 10 to 1 at a pressure of 500 pounds per square inch.

It was found that with silica-alumina components in the range of about 20 D+L to about 45 D+L the yields of reformed product (volume percent five-carbon atom and higher hydrocarbons based on fresh feed), for any particular octane number level, were equal and at a maximum. With silica-alumina components having D+L ratings above 45 the yields were below this maximum for any constant octane number level. Table I shows the percent yield deviation from the maximum for the catalysts prepared and tested as described above for two different octane number levels.

Table I

Clear Octane Number CFRR (ASTM Method D908-53)	D+L of the Silica-Alumina Component	Percent Decrease in Yield from Maximum
85.0	27	0
85.0	31	0
91.7	38	0
85.0	45	0
85.0	60	2.6
91.7	70	4.7
85.0	82	8.4
85.0	88	10.6
91.7	93 Unsteamed	12.1

These data are plotted in Figure 1 of the drawings. It is to be noted that the catalysts produced from silica-alumina components having D+L ratings between about 20 and about 45 all give the maximum yield at the same octane level, and consequently the slope of the curve in this area is zero. With catalysts produced from silica-alumina components having D+L ratings between about 45 and 65 the yields obtained drop below the maximum and accordingly the slope of the curve increases in this area to a maximum at about 65 D+L. Catalysts prepared from components having D+L ratings greater than 65 and up to the 90–95 level (corresponding to a freshly prepared, unsteamed component) produce yields which deviate from the maximum in direct proportion to the D+L rating of the component and hence from 65 D+L to 90–95 D+L the curve forms a second straight line with a maximum slope. The straight line portions of the curve have been extended in the form of dotted lines to show the area of deviation from the constant slope lines.

It is apparent from this curve that catalysts prepared from components ranging between 20 and 45 D+L are capable of completely controlling the hydrocracking reaction and maintaining a balance between it and the other reforming reactions, while between 45 and 65 some ability to control the hydrocracking reaction is lost. Catalysts prepared from components having D+L ratings in excess of 65, however, were found to have no ability to control the hydrocracking reaction as evidenced by the fact that the loss of yield varies directly with the activity of the base component. Accordingly, this curve demonstrates the necessity for using acidic metal oxide components having D+L ratings below 65, as measured by the Birkhimer et al. method.

Catalysts prepared from components having D+L ratings less than 20 are not preferred since they do not have sufficient activity to produce the octane level gasolines required by present day automotive engines.

In the following examples a number of catalysts were prepared both according to prior art methods and according to the method of the instant invention. In order to show the superior stability of the catalysts of the instant invention, all of the catalysts were tested according to a standard reforming test procedure in the laboratory since it was obviously impractical to test every experimental catalyst in a full scale or commercial reforming operation.

In the laboratory reforming stability test a 75 cc. portion of the catalyst is placed in a fixed bed in the form of discrete pellets (8–12 mesh, U.S. standard) and an East Texas distillate having the following properties.

ASTM distillation:

Overpoint	° F.	180
50 percent	° F.	250
95 percent	° F.	330
End point	° F.	365

Clear Octane Number (ASTM Method D908–53)	55
API gravity at 60° F	56.5

is passed thereover under the following conditions:

Inlet temperature to the catalyst bed and outlet temperature from the catalyst bed is maintained at 875° F. for 24 hours, and then is raised to 940° F. for the remainder of the test; hourly liquid space velocity is 3; pressure is 500 pounds per square inch; hydrogen to hydrocarbon mol. ratio is 10 to 1. Samples of product are taken at regular time intervals during the run, and their octane numbers determined. The difference in octane number of the product after the catalysts have been on stream for 72 hours and after 200 hours at a constant average catalyst bed temperature is utilized as a part of the measure of the catalyst stability as will be shown hereinafter.

The reactor consists of a metal tube surrounded by heaters to maintain approximately isothermal conditions. A thermocouple well is placed at the center of the reactor so that the temperature of the catalyst bed can be determined throughout its length. It is a characteristic of the reforming process using a fixed bed reactor with a platinum on metal oxide component type catalyst that at a point near the top of the catalyst bed the temperature of the catalyst will be at a minimum, which temperature is somewhat lower than either the inlet or outlet temperatures heretofore mentioned. The explanation for this minimum in the catalyst bed temperature is relatively simple. As has been noted, one of the most important and also most rapid reactions in catalytic reforming is the dehydrogenation reaction, i.e., the conversion of naphthenes to aromatics. This reaction is highly endothermic, that is, it utilizes rather large amounts of heat. Inasmuch as it is a reaction that proceeds rapidly, it reaches its maximum rate at a point near the top of the catalyst bed and, under the specified experimental conditions, it removes heat faster than it can be supplied with the result there will be a minimum in the temperature "profile" of the catalyst bed at the point where the dehydrogenation reaction is at its maximum. With a catalyst of high stability, since the heat input and other conditions are constant, this "minimum bed temperature," as it will be referred to hereinafter, will remain at nearly a constant value. Obviously, if the catalyst's ability to promote the dehydrogenation reaction declines during its life, less dehydrogenation will occur and therefore less heat will be utilized, with the result the minimum bed temperature will rise. Consequently, the increase in minimum bed temperature gives very important information as to the stability of the catalyst under test.

As noted hereinbefore, the difference in octane value of the product after the catalyst has been on stream for 72 hours and after 200 hours is noted. This difference, while of obvious value in judging stability, might possibly be misleading if used as the sole criterion for stability. It might be misleading for example, if a catalyst started out with good over-all reforming characteristics, but later lost its ability to dehydrogenate while greatly increasing the hydrocracking reaction. The hydrocracking reaction will of course raise octane values, but at the expense of producing large amounts of low molecular weight compounds not useful in gasoline. Thus, in the above example, while the octane decrease might be small indicating a relatively stable catalyst, actually such a catalyst could have relatively poor stability. Therefore, by using a combination of minimum bed temperature change and octane value change over the period of test, a much more reliable and accurate measure of catalyst stability for reforming can be obtained.

The above described test gives an accelerated decrease in stability because of the extremely severe temperature levels used. In commercial plant operation, of course, much lower severities are used hence the decrease in octane number with time and decrease in the dehydrogenation reaction with time are considerably more gradual. Thus, although in the laboratory test octane number declines of several units may be experienced in the 128 hour test period, such declines require weeks or months in actual commercial operation. The correlation of the accelerated laboratory stability test has been found to be very good, however, with regular plant runs. Inasmuch as the changes noted in the short time period of the laboratory test require much longer periods in plant scale operation, it follows that small differences between catalysts as measured in the laboratory test will represent large differences in plant operation.

A method has been devised which not only makes use of the difference found between actual catalysts tested in laboratory and expresses such differences in terms of relative stabilities, but which also compares the relative stabilities of actual catalysts with a theoretical completely stable catalyst as a standard.

If a catalyst were completely stable it would, of course, show neither an octane number decrease nor a minimum bed temperature increase when tested in the above described laboratory reforming stability test. For purposes of the comparison, this standard or "perfect" catalyst is assigned a total relative stability number of 100. Actual catalysts obviously will have total relative stability numbers less than the theoretical value of 100, since they will show a minimum bed temperature increase and an octane number decrease. It is to be noted, however, that both factors contribute to the total stability of the catalyst; accordingly, a partial relative stability number is given to each, the sum of such partial relative stability numbers being the total relative stability number.

Since, as has been pointed out, dehydrogenation reaction stability is of primary importance, the relative contribution of dehydrogenation reaction stability (measured by minimum bed temperature increase) to the total relative stability is greater than the contribution of the octane number stability to the total relative stability. In order to properly weigh these relative contributions, a value of 60 was selected for the partial relative stability number of the dehydrogenation reaction stability contribution and a value of 40 for the partial relative stability number of the octane number in the case of the standard catalyst. These partial relative stability numbers for actual catalysts are in the same ratio, but obviously less than the standard values of 60 and 40, respectively.

It has been found that a commercially acceptable catalyst when tested by the laboratory method showed a minimum bed temperature increase between the 72nd hour and 200th hour of 6° F., and an octane number decline during the same time period of 3. This present commercially acceptable catalyst was assigned a total relative stability number of 50.

From these data the plots in the accompanying drawings were constructed.

Referring now to Figure 2 of the drawings where the partial relative stability number for the dehydrogenation reaction stability contribution is plotted along the ordinate and the minimum bed temperature increase is plotted along the abscissa, the abovementioned standard catalyst, designated "Catalyst S," is located, of course, at 60 on the ordinate of the plot, as shown. The abovementioned commercially acceptable catalyst, designated "Catalyst A," which was prepared by impregnating a silica-alumina component having a D+L of about 42 with chloroplatinic acid to give a finished catalyst containing 0.45 percent platinum (details of preparation are the same as details for "Catalyst No. 1," below, except platinum content) having a minimum bed temperature increase of 6, has a partial relative stability number for the dehydrogenation reaction stability contribution of 30 calculated by: 60/100 (dehydrogenation reaction contribution) times 50 (total relative stability number of commercially acceptable catalyst) equals 30.

Thus, the point for Catalyst A on the plot of Figure 2 is located.

Referring to Figure 3 of the drawings where the partial relative stability number for the octane number stability contribution is plotted along the ordinate and octane decline is plotted along the abscissa, the above-mentioned standard, Catalyst S, is located at 40 on the ordinate of the plot, as shown. The commercially acceptable catalyst, Catalyst A, having an octane number decline of 3, has a partial relative stability number for the octane number contribution of 20 calculated by: 40/100 times 50 equals 20. Thus, the point for Catalyst A is located on the plot of Figure 3.

Correlation lines, C and D in Figures 2 and 3 respectively, are drawn through the points located on the plots. Having determined these lines, the stability of each catalyst can be compared with the stability of every other catalyst by utilizing the data obtained in the standard reforming stability test.

Obviously, if the correlation lines are extended below the points for Catalyst A on the plots, they can be used to rate catalysts somewhat poorer than commercially acceptable catalysts.

In order to prepare a series of catalysts for stability comparison, a quantity of a fresh commercial silica-alumina cracking catalyst was prepared as described in Example I above in the form of cylindrical pellets 3/16 inch in diameter and 3/16 inch high having a D+L rating of 93. Several portions of this component were treated with steam at a pressure of 150 pounds per square inch and at a temperature of 1050° F. for various times until the D+L of the silica-alumina was reduced to the various values indicated in the examples.

EXAMPLE II

A portion of the silica-alumina component prepared as described above having a D+L of 42.4 was contacted with an 0.026 molar aqueous chloroplatinic acid solution, 1.2 cc. of solution being used per gram of pellets. This solution was allowed to remain in contact with the silica-alumina for about 24 hours at approximately 210° F. to 212° F. The impregnated pellets of silica-alumina were then dried in a stream of nitrogen at a temperature somewhat above 212° F., following which the platinum was reduced to the metallic state with hydrogen at 250° F. The platinum content of the finished catalyst was 0.48 percent by weight. This catalyst, designated at Catalyst No. 1, corresponds to a commercial reforming catalyst.

EXAMPLE III

A second portion of the silica-alumina component having a D+L of 42.4 was treated with an 0.0214 molar aqueous solution of platinous tetramminochloride, $[Pt(NH_3)_4]Cl_2$, together with sufficient ammonium hydroxide to raise the pH of the solution to 11.1, the amount of solution being 1.2 cc. per gram of silica-alumina. The ammonium hydroxide was added since, in order to impregnate an acidic metal oxide component with this compound, it is necessary to raise the pH to a high level. The solution was held in contact with the silica-alumina for 20 hours at 210° F. to 212° F. Then the solution was drained from the impregnated silica-alumina component, and the component dried at a temperature in excess of 250° F. in a stream of nitrogen. Finally, the platinum on the catalyst was reduced to the metallic state with hydrogen at a temperature of about 950° F. This catalyst, Catalyst No. 2, contained 0.454 percent by weight of platinum.

EXAMPLE IV

A third portion of the silica-alumina component having a D+L of 40.3 was treated with an 0.0203 molar aqueous solution of platinous tetramminohydroxide, $[Pt(NH_3)_4](OH)_2$, for 18 hours at 212° F. The amount of solution used was 1.2 cc. per gram of silica-alumina. The solution was drained from the impregnated silica-alumina component and the component then was dried in a stream of nitrogen at a temperature in excess of 250° F. The platinum was reduced to the metallic state with hydrogen at about 950° F. The finished catalyst contained about 0.465 percent of platinum by weight and is designated as Catalyst No. 3.

EXAMPLE V

A fourth portion of the silica-alumina component having a D+L of 45 was treated with platinous tetramminohydroxide by the method described in Example IV to give a finished catalyst, Catalyst No. 4, having 0.355 percent by weight of platinum.

EXAMPE VI

A fifth portion of the silica-alumina component having a D+L of 40.3 was contacted with an 0.0276 molar aqueous solution of platinous tetramminohydroxide in the proportions of 1.2 cc. of solution per gram of silica-alumina component. The solution was held in contact with the component for 18 hours at 212° F. The impregnated silica-alumina pellets were drained and dried at 250° F., then the dried impregnated pellets were calcined with air at a temperature of 650° F. to 700° F. for two hours. The finished catalyst, Catalyst No. 5, contained 0.620 weight percent of platinum.

EXAMPLE VII

A sixth portion of the silica-alumina component having a D+L of 59.1 was treated with an 0.036 molar aqueous solution of platinous tetramminohydroxide for 18 hours at 212° F. The amount of solution used was 1.2 cc. per gram of silica-alumina. The solution was drained from the impregnated component and the component was then dried at about 250° F. The dried impregnated pellets were then calcined with air at 650° F. to 700° F. to convert the platinum component to metallic platinum. The finished catalyst, Catalyst No. 6, contained 0.79 percent by weight of platinum.

Each of the catalysts prepared above was tested by the above described laboratory reforming stability test. It should be noted that each of the catalysts raised the clear octane number of the standard charge stock from 55 to about 90 to 92 (at the 72 hour point) as measured by ASTM Method D908–51. The results of the test and the stabilities found from Figures 2 and 3 for the catalysts are set forth in Table II:

Table II

Catalyst Number	Impregnating Compound and Platinum Content of Finished Catalyst	Decrease in Octane Number	Increase in Minimum Bed Temp., ° F.	Total Stability Number
1	H_2PtCl_6 0.48% Pt	2.5	6	53
2	$[Pt(NH_3)_4]Cl_2$ 0.454% Pt	4.0	6	43
3	$[Pt(NH_3)_4](OH)_2$ 0.465% Pt.	2.0	1	82
4	$[Pt(NH_3)_4](OH)_2$ 0.355% Pt.	3.1	2	69
5	$[Pt(NH_3)_4](OH)_2$ 0.62% Pt.	1.4	1	86
6	$[Pt(NH_3)_4](OH)_2$ 0.79% Pt.	1.6	0	89.5

It is evident from the above data that the use of platinous tetramminohydroxide for impregnating an acidic metal oxide component produces a catalyst having a very markedly improved stability. For example, a catalyst of the present invention shows a 60 percent increase in stability over present commercially acceptable catalysts prepared by impregnation with chloroplatinic acid, comparing catalyst Nos. 3 and 5 with Catalyst No. 1. The catalysts of the present invention show about twice the stability of catalysts prepared by impregnation with platinous tetramminochloride, Catalyst No. 2.

The data also show that a catalyst prepared according to the instant invention is 30 percent more stable

than a commercial catalyst containing over 30 percent more platinum, comparing Catalyst No. 4 with Catalyst No. 1. Consequently, the present invention permits very important savings in catalyst cost both by using less platinum on the catalyst and by providing catalysts having greatly increased life.

In order to demonstrate further the superiorty of the instant invention, comparative runs were made in a commercial catalytic reforming plant having a capacity of about 2500 barrels per day.

This plant was first operated with the best available regular commercial catalyst prepared according to the method of Example II wherein chloroplatinic acid was used for impregnating the silica-alumina. Then the plant was operated on a catalyst of the instant invention prepared by the method of Example VII wherein platinous tetramminohydroxide was employed in impregnating the silica-alumina base. The charge stock to the plant was a blend of Western and Pennsylvania straight run naphthas having the following properties.

ASTM distillation:		
Overpoint	° F.	111
50 percent	° F.	255
90 percent	° F.	349
End point	° F.	396
Clear octane number (ASTM Method D908–51)		52
API gravity at 60° F		63.7

The operating conditions were: 600 p.s.i. pressure, 17:1 hydrogen to hydrocarbon ratio, and 3 space velocity. The average reactor inlet temperature was varied to produce regular and premium gasoline grades.

With the regular commercial catalyst the average reactor inlet temperature was raised to 930° F. in an attempt to make a 95 octane product (with 3 cc. TEL/gallon), however, the maximum octane obtained under these conditions was 94.0 octane (with 3 cc. TEL.) and the octane decreased rapidly with time at this temperature showing that the catalyst was not stable. After operation under these conditions for three days, the temperature was lowered to 885° F. to produce regular grade gasoline of 89–90 octane (with 3 cc. TEL/gallon). It was necessary to raise the average reactor inlet temperature by incremental amounts to maintain this octane level until a final temperature of 935° F. was reached after 27 additional days of operation at which time the catalyst was completely deactivated and required regeneration. Following regeneration a second attempt was made to make premium grade gasoline, 95 octane, but even at temperatures as high as 935° F. to 940° F. the product was only 93 octane (with 3 cc. TEL/gallon).

Following the test run with the regular commercial catalyst, a second test run was conducted wherein the same feed stock previously described was treated with the above mentioned catalyst of the present invention under substantially the same conditions of pressure, hydrogen to hydrocarbon ratio and space velocity employed in the first test run. As in the first test run the average reactor inlet temperature was varied to produce regular and premium grade gasoline.

After 10 days of operation at a temperature of about 860° F., during which period regular grade gasoline having an octane rating between 89 and 91 was produced, the average reactor inlet temperature was raised to 910° F. to produce a 95 octane (with 3 cc. TEL/gallon) gasoline. Following 4 days of operation at this premium octane level, the temperature was intermittently lowered and raised for a further period of 46 days, during which period regular and premium grade gasolines were alternately produced at average temperatures the same as or below those employed in the beginning of the run, i.e. 860° F. for regular and 910° F. for premium. At the end of the stated period of alternate operation which covered a total of 61 days a slightly higher temperature was required to produce 95 octane gasoline, however, after 5 days at this level, about 920° F., the temperature was lowered to produce regular grade gasoline at 860° F. and operation under these conditions was being maintained after 93 days.

The last run described clearly demonstrates the phenomenal stability of the catalyst of the present invention. It is to be observed from the results of this run that after several months of operation at normal refinery practice, ie. alternate production of regular and premium gasolines with the amount of premium being produced being between 20 percent and 30 percent of the total, the novel catalyst of this invention showed practically no deactivation as evidenced by the fact that the temperatures required to obtain regular and premium grade gasolines were substantially the same throughout the entire period of operation. In addition, the temperatures required to produce either regular or premium grade gasoline were substantially lower when using the catalyst of the instant invention as contrasted to the commercial catalyst prepared by depositing chloroplatinic acid on the silica-alumina base, which catalyst, of course, was not capable of producing premium grade gasoline from this feed stock.

Furthermore, the test run on the platinous tetramminohydroxide impregnated catalyst of this invention had a better yield-octane relationship than the regular commercial catalyst. At the premium grade level, 95 octane, the instant catalyst gave a 3 percent better yield of gasoline than the regular commercial catalyst and at regular grade gasoline level, 90 octane, the instance catalyst gave about a 2 percent higher yield of gasoline than the regular commercial catalyst. The comparison at the premium grade level could be obtained only by extrapolation of the yield-octane curve for the regular commercial catalyst since it, of course, only produced gasoline of 94 octane with this feed stock during the first test run.

Accordingly, these actual plant runs prove conclusively that the catalysts of the instant invention not only have a stability far superior to previously known catalysts, but also are capable of producing a higher octane level product with a higher yield than possible with the prior art catalysts.

The method of the instant invention has been found to be effective in the preparation of reforming catalysts for treatment of petroleum distillates, such as light hydrocarbons, naphtha, gasoline and kerosine, and particularly gasoline fractions. The fractions may have an initial boiling point within the range of 50° F. to 90° F. and an end boiling point of about 425° F. to 560° F.

It is preferred when reforming petroleum distillates boiling in the gasoline-kerosine range to utilize reaction temperatures within the range of 600° F. to 1000° F., pressures of from 100 to 1000 pounds per square inch, liquid hourly space velocities of from 0.1 to 10 and hydrogen to hydrocarbon mol. ratios of from 1 to 20 mols. of hydrogen per mol. of hydrocarbon.

We claim:

1. A method of manufacturing a catalyst which comprises impregnating an acidic metal oxide component with an aqueous solution of platinous tetramminohydroxide, drying the impregnated acidic metal oxide component and converting the platinum impregnated on the acidic metal oxide component to the metal, said acidic metal oxide component being characterized by having a catalytic cracking activity within a range between 20 and 65 as compared with a theoretical maximum catalytic cracking activity of 100 and practicable maximum catalytic cracking activity of between 90 and 95 on a distillate-plus-loss scale for the measurement of the catalytic cracking activity of a cracking catalyst.

2. A method of manufacturing a catalyst which comprises contacting an acidic metal oxide component with an aqueous solution of platinous tetramminohydroxide at an elevated temperature to impregnate the acidic metal oxide component, drying the impregnated acidic metal

oxide component, and converting the platinum impregnated on the acidic metal oxide component to the metal, said acidic metal oxide component being characterized by having a catalytic cracking activity within a range between 20 and 65 as compared with a theoretical maximum catalytic cracking activity of 100 and a practicable maximum catalytic cracking activity of between 90 and 95 on a distillate-plus-loss scale for the measurement of the catalytic cracking activity of a cracking catalyst.

3. A method of manufacturing a catalyst which comprises impregnating silica-alumina with an aqueous solution of platinous tetramminohydroxide, drying the impregnated silica-alumina and converting the platinum impregnated on the silica-alumina to the metal, said silica-alumina component being characterized by having a catalytic cracking activity within a range between 20 and 65 as compared with a theoretical maximum catalytic cracking activity of 100 and a practicable maximum catalytic cracking activity of between 90 and 95 on a distillate-plus-loss scale for the measurement of the catalytic cracking activity of a cracking catalyst.

4. The catalyst prepared by the method of claim 3.

5. A method of manufacturing a catalyst which comprises contacting silica-alumina with an aqueous solution of platinous tetramminohydroxide at an elevated temperature to impregnate the silica-alumina, drying the impregnated silica-alumina and converting the platinum impregnated on the silica-alumina to the metal, said silica-alumina component being characterized by having a catalytic cracking activity within a range between 20 and 65 as compared with a theoretical maximum catalytic cracking activity of 100 and a practicable maximum catalytic cracking activity of between 90 and 95 on a distillate-plus-loss scale for the measurement of the catalytic cracking activity of a cracking catalyst.

6. A process for reforming a petroleum distillate fraction boiling within the gasoline-kerosine range to increase the anti-knock value thereof which comprises subjecting said fraction to contact at reforming conditions in the presence of hydrogen with a catalyst prepared by contacting at an elevated temperature a silica-alumina component with an aqueous solution of platinous tetramminohydroxide to impregnate the silica-alumina, drying the impregnated silica-alumina and converting the platinum impregnated on the silica-alumina to the metal, the platinum being in an amount between 0.1 to 2.5 percent by weight of the final catalyst, said silica-alumina component being characterized by having a catalytic cracking activity within a range between 20 and 65 as compared with a theoretical maximum catalytic cracking activity of 100 and a practicable maximum catalytic cracking activity of between 90 and 95 on a distillate-plus-loss scale for the measurement of the catalytic cracking activity of a cracking catalyst.

7. A process for reforming a gasoline fraction to increase the anti-knock value thereof which comprises subjecting said fraction to contact at a temperature within the range of 600 to 1000° F., a pressure of from 100 to 1000 pounds per square inch and a liquid hourly space velocity of from 0.1 to 10, in the presence of from 1 to 20 mols. of hydrogen per mol. of hydrocarbon with a catalyst prepared by contacting at an elevated temperature a silica-alumina component with an aqueous solution of platinous tetramminohydroxide to impregnate the silica-alumina, drying the impregnated silica-alumina and converting the platinum impregnated on the silica-alumina to the metal, the platinum being in an amount between 0.1 to 2.5 percent by weight of the final catalyst, said silica-alumina component being characterized by having a catalytic cracking activity within a range between 20 and 65 as compared with a theoretical maximum catalytic cracking activity of 100 and a practicable maximum catalytic cracking activity of betwen 90 and 95 on a distillate-plus-loss scale for the measurement of the catalytic cracking activity of a cracking catalyst.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,884,374 April 28, 1959

James E. Connor, Jr., et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 11, line 47, for "designated at" read -- designated as --; column 14, line 19, after "catalyst" strike out "pre-".

Signed and sealed this 18th day of August 1959.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

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Commissioner of Patents