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CONVERSION OF HYDROCARBONS WITH PLATINUM COMPOSITE CATALYST

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This invention relates to the conversion of hydrocarbons and to the preparation and use of a novel catalyst in the conversion of hydrocarbons.

In conversion processes of the type wherein carbon formation is a matter of great concern, the commercial success of the process in many cases depends upon the characteristics of the catalyst to minimize carbon formation but at the same time effect the desired conversion. Typical examples of pertinent processes include those in which cracking of carbon to carbon bonds occurs as, for example, in the cracking of higher boiling oils or gases to produce lower boiling products, either in the presence or absence of hydrogen. When hydrogen is present in the cracking operation, the process is generally referred to as hydrocracking.

Another process in which the formation of carbon is of considerable concern is the reforming process which is effected either in the presence or absence of hydrogen. In this process the desired reactions include dehydrogenation, isomerization, hydrogen transfer, etc. and a controlled amount of cracking. As will hereinafter be set forth in detail the amount of cracking must be controlled both in quantity and in quality. However, it has been found that along with cracking the formation of carbon likewise occurs. The deposition of carbon on the catalyst is undesirable because it inactivates the catalyst and interferes with the desired conversion.

The carbonaceous deposit on the catalyst includes compounds of carbon and hydrogen and, in the interest of simplicity, is being referred to in the present specification and claims as carbon. The present invention is directed to a novel catalyst composition which will minimize the formation of carbon on the catalyst, and to the use of this catalyst in the conversion of hydrocarbons.

In one embodiment the present invention relates to a conversion process which comprises subjecting a hydrocarbon to conversion in the presence of a catalyst comprising alumina, platinum, combined halogen and not more than about 1% by weight of an oxide of the group consisting of an alkaline earth metal or magnesium.

In a specific embodiment the present invention relates to a process for the reforming of a gasoline fraction which comprises subjecting said gasoline fraction to contact at reforming conditions with a catalyst comprising alumina, combined halogen in an amount of from about 0.1% to about 8% by weight, platinum in an amount of from about 0.01% to about 1% by weight, and an alkaline earth metal or magnesium in an amount of from about 0.01% to about 1% by weight.

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In another specific embodiment the present invention relates to a method of manufacturing a catalyst which comprises precipitating alumina from aluminum chloride, washing to substantially remove soluble impurities, commingling a halogen therewith, compositing platinum therewith, and commingling an alkaline earth metal or magnesium compound with the composite.

As hereinbefore set forth, in the reforming operation, a controlled amount of hydrocracking is desired, along with the dehydrogenation of naphthenic hydrocarbons to produce aromatics, the cyclization of the straight chain paraffinic hydrocarbons to form aromatics, the isomerization of straight chain aliphatic hydrocarbons, hydrogen transfer reactions, etc. The cracking or splitting of carbon to carbon bonds must be controlled both in quantity and in quality. It has been found that the selected cracking results in improved reformed products. The lower molecular weight hydrocarbons have higher octane numbers, and also when the gasoline charging stock contains components boiling above about 400° F., the higher boiling components are cracked to lower boiling components. The overall results of the selective cracking is a reformate of improved properties. However, the cracking must be controlled in quantity so as not to produce an excess of normally gaseous products which can not be used in the reformate and, therefore, would result in lower reformate yields. Excessive cracking also results in the formation of larger carbon deposits on the catalyst.

It has been found that a particularly suitable catalyst for use in reforming operations comprises alumina, platinum and combined halogen in specific amounts. The use of platinum-containing catalyst has been of limited commercial acceptance because of the high cost of platinum. It has been found that exceptionally good catalysts containing small amounts of platinum may be made in accordance with the present invention. The amount of platinum is generally within the range of from about 0.01% to about 1% by weight, although in some cases it may range up to about 10% by weight of the alumina. The presence of the combined halogen in an amount ranging from about 0.1% to about 8% by weight enhances the activity and life of the catalyst. When the halogen comprises fluorine, it is present in an amount of from about 0.1% to about 3% by weight and when the catalyst comprises chlorine, it is present in an amount of from about 0.2% to about 8% by weight. In some cases, the halogen may comprise a mixture of fluorine and chlorine, the total thereof being within the range of from about 0.1% to about 8% by weight of the alumina.

It has been found that the presence of an alkaline earth metal or magnesium compound serves to reduce the amount of carbon formed during the reforming operation. Of the alkaline earth metal compounds, the oxides of calcium, strontium and barium are preferred. Magnesium has many properties which resemble those of the alkaline earth metals and in many cases has been loosely referred to as an alkaline earth metal. In some cases it has been listed in periodic table arrangements in the left hand column of Group II along with the alkaline earth metals. For example, see "The Physical Basis of Things," page 96, by J. A. Eldridge. In the present invention magnesium has shown the same properties as the alkaline earth metals in reducing carbon formation and, therefore, it is being included in a Markush grouping in the claims of the present application.

In order to obtain improved results with the low platinum concentrations, it has been found that alumina shows unexpected advantages for use in the catalyst composite. The alumina apparently enters into some peculiar association, either chemical or physical, with the platinum and/or halogen. The exact state of the platinum in the catalyst composite is not completely established but is believed to be, at least in part, in a combined state with the alumina and/or halogen. However, it is understood that the platinum, at least at some time during preparation or use, may be present as free platinum, and the use of the term "platinum" is intended to include both the combined platinum and the free platinum. Similarly, it is believed that the alkaline earth metal or magnesium may be present either as the free metal or as a compound, particularly oxide, which may be associated with the other components of the catalyst, either chemically or physically.

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

After the alumina has been formed, it is generally washed to remove soluble impurities. Usual washing procedures comprise washing with water, either in combination with filtration or as separate steps. It has been found that filtration of the alumina is improved when the wash water includes a small amount of ammonium hydroxide. The severity of the washing may vary, depending upon whether all or part of the chlorine is to be retained in the catalyst composite. When chlorine is not desired, the alumina is washed thoroughly to remove substantially all of the chlorine. On the other hand, if a part of the chlorine is to be retained in the catalyst, the washing is less severe. In general, it is preferred to wash the alumina thoroughly and, if it is desired to add chlorine, it is added as a separate step because better control of the amount of the chlorine is obtained in this manner.

The alumina so prepared may be dried, and formed into particles of uniform or irregular size and shape prior to the addition of the other components, or all or a portion of the other components may be added, and the catalyst subsequently formed into particles. In a preferred embodiment the halogen is incorporated into the alumina before forming into particles, and this may be accomplished by adding the halogen in the form of an acid such as hydrogen fluoride, hydrogen chloride, hydrogen bromide and/or hydrogen iodide. In some cases, the volatile salts such as ammonium fluoride, ammonium chloride, etc. may be employed. In any event, the amount of halogen will be within the range hereinbefore set forth.

The platinum may be added to the alumina either before or after the alumina is formed in the particles and either before or after the halogen or other components are commingled therewith. As hereinbefore set forth, the preferred method is to add the halogen to the alumina, form into particles, and then add the platinum. In this method the platinum is preferably added in the presence of ammonium hydroxide. A particularly preferred method is to commingle chloroplatinic acid with ammonium hydroxide to form a mixture having a pH within the range of from about 5 to about 10 and preferably from about 8 to about 10, and then commingle this mixture with the preformed particles. It is understood that the ammonium hydroxide or platinum compound first may be added to the preformed particles and then the other component may be added, and also that these components may be composited either as cold or hot solutions.

In another embodiment of the invention and particularly when the platinum is added to the alumina, with or without halogen, prior to forming the same into particles of uniform size and shape, a preferred method is to form a separate solution of chloroplatinic acid and hydrogen sulfide, and then to utilize this solution for impregnating the alumina.

The use of ammonium hydroxide when adding the platinum compound to the preformed pills or the use of the chloroplatinic acid-hydrogen sulfide mixture when adding the platinum compound to the wet alumina-halogen composite is definitely advantageous in order to obtain even distribution of the platinum throughout the catalyst. Regardless of the method of compositing the platinum, it is understood that the amount of platinum in the final catalyst will be within the range hereinbefore set forth.

The alkaline earth metal or magnesium compound may be added either before or after the other components and either before or after all or a part of the catalyst composition has been formed into particles of uniform size and shape. In general, it is preferred to add the alkaline earth metal or magnesium after the washing and filtration step in order that these compounds will not be removed. Thus, the alkaline earth metal or magnesium is preferably added during the final stages or catalyst preparation.

The alkaline earth metal or magnesium may be added in any suitable manner and usually will be added in the form of a compound which all decompose on heating to form the oxide. Thus, these compounds may be added in the form of the nitrate, hydroxide, acetate, etc. Usually the

alkaline earth metal or magnesium compound will be added in the form of an aqueous solution in order to effect uniform distribution on the surface and within the interior of the catalyst particles. However, it is understood that any other suitable method of intimately disposing these components within the catalyst may be employed. As hereinbefore set forth, it is an essential feature of the present invention that the amount of the alkaline earth metal or magnesium compound, determined as calcium, strontium, barium, magnesium, etc. must not exceed 1% by weight of the alumina. While the use of these compounds in amounts of less than 1% by weight and generally within the range of from about 0.01% to about 1% by weight will serve to minimize carbon formation without adversely affecting the activity of the catalyst, the use of these compounds in amounts greater than 1% will exert a harmful effect on the activity of the catalyst and will serve to reduce the desired conversion.

Regardless of when the composite is to be formed into particles of uniform size and shape, this is readily accomplished by partially drying at a temperature of from about 200° to about 500° F. for a period of about 2 to 24 hours or more to form a cake. A suitable lubricant such as stearic acid, rosin, hydrogenated coconut oil, graphite, etc., is added to the dried and ground cake and the composite is formed into pills of uniform size and shape in any suitable pelleting apparatus. The pills may range from a size of about $\frac{1}{16}$'' x $\frac{1}{16}$'' to $\frac{1}{4}$'' x $\frac{1}{4}$'' or more. Pills of uniform size and shape also may be formed by extrusion methods. When desired, the catalyst may be formed into particles of irregular size and shape by grinding. When the pills are formed prior to the addition of the platinum, the pills preferably are calcined in air at a temperature of from about 1000° to about 1400° F. for a period of from 1 to 8 hours or more. However, after the platinum has been composited with the alumina, the catalyst should not be calcined at a temperature above about 1000° F. and preferably is calcined in air at a temperature of from about 500° to about 1000° F. for a period of about 2 to 12 hours or more. In one embodiment of the invention the catalyst may be reduced in the presence of hydrogen at a temperature of below about 1000° F. for a period of about 2 to 12 hours or more and then calcined in the presence of air at a temperature of from about 500° to about 1000° F. for a period of about 2 to 12 hours or more.

It is a particular feature of the present invention that the novel catalyst composite will reduce carbon formation and, therefore, the catalyst will have a long life. However, after long periods of service, it may be necessary to regenerate the catalyst and this may be accomplished by treatment with air or other oxygen containing gas to burn the carbonaceous deposit therefrom. In general, it is preferred to control the regeneration temperature not to exceed about 1000° F. and preferably the regeneration is effected at a temperature within the range of from about 600° to about 900° F.

The conditions of operation for effecting the conversion of hydrocarbons will depend upon the particular reactions desired. Reforming of gasoline will be effected at a temperature of from about 600° to about 1000° F., a pressure within the range of from about 50 to about 1000 pounds per square inch and at a weight hourly space velocity of from about 0.5 to about 10. The weight hourly space velocity is defined as the weight of oil per hour per weight of catalyst in the reaction zone. The reforming operation is preferably effected in the presence of hydrogen and the amount of hydrogen present in the reaction zone generally will be within the range of from about 0.5 to about 10 mols of hydrogen per mol of hydrocarbon. The reforming process will be operated under conditions to produce hydrogen so that the hydrogen so produced may be recycled within the process and thus obviate the necessity of introducing hydrogen from an extraneous source except at the start of the process.

It is understood that the reforming process is applicable for the treatment of a full boiling range gasoline or any selected fraction thereof, and that reference to a gasoline fraction in the present specifications and claims is intended to mean either the full boiling range gasoline or any selected fraction thereof.

As hereinbefore set forth, the catalyst of the present invention is also particularly suitable for use in hydrocracking reactions and these are generally effected at temperatures of from about 500° to about 900° F. The catalyst of the present invention may also find utility in effecting dehydrogenation reactions and will be utilized in such operations at temperatures of from about 800° to about 1000° F.

The process of the present invention may be effected in any suitable equipment. A particularly suitable process comprises the 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 in the process. Other suitable units in which the process may be effected include the fluidized type process in which the hydrocarbons and catalyst are maintained in a state of turbulence under hindered settling conditions in a reaction zone, the compact moving bed process in which the catalyst and hydrocarbons are passed either concurrently or counter-currently to each other, and the suspensoid process in which the catalyst is carried into the reaction zone as a slurry in the hydrocarbon oil.

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

Catalyst No. 1 was prepared by adding ammonium hydroxide to aluminum chloride to precipitate aluminum hydroxide. The aluminum hydroxide was washed with ammoniated water. Hydrogen fluoride was added to the wet alumina in an amount to form a final catalyst containing 0.75% of fluorine by weight. A colloidal suspension of chloroplatinic acid and hydrogen sulfide was separately prepared and was added to the aluminum hydroxide-fluorine composite in an amount to form a final catalyst containing 0.3% of platinum by weight. The composite was dried, ground into granules and calcined at a temperature of 932° F. for 3 hours.

Catalyst No. 2 was prepared in substantially the same manner as catalyst No. 1 except that subsequent to the addition of the colloidal solution of chloroplatinic acid and hydrogen sulfide and prior to drying, calcium nitrate was added

in an amount of 0.1% by weight of calcium based on the alumina. The catalyst was then dried and calcined as set forth in the preparation of catalyst No. 1.

These catalysts each were separately used in the reforming of a Mid-Continent naphtha having a boiling range from 182° to 402° F. The reforming was effected at a temperature of 851° F. catalyst temperature, a pressure of 500 pounds per square inch, a weight hourly space velocity of 2 and a hydrogen:hydrocarbon ratio of 3:1. Each of the runs was conducted for 3 days, and the results of the third day of operation are shown in the following table, along with additional analysis of the charging stock.

Table I

	Charge	Catalyst 1	Catalyst 2
Yield, weight percent of charge		93.7	93.7
Product:			
Specific Gravity @ 60° F	0.7612	0.7682	0.7783
Octane Number, Motor Method	34.6	78.2	75.0
Octane Number, Research Method	34.8	84.6	81.3
Percent Aromatics	6	53	49
Carbon, Weight Percent of Catalyst		2.46	0.76

It will be noted from the data in the above table that catalyst No. 2 containing 0.1% of calcium produced only 0.76% by weight of carbon, as compared to a value of 2.46% of carbon for the catalyst No. 1 not containing calcium.

EXAMPLE II

Catalyst No. 3 was prepared by adding ammonium hydroxide to aluminum chloride to precipitate aluminum hydroxide, washing to remove soluble impurities, adding hydrogen fluoride in an amount to form a final catalyst containing 0.3% fluorine, drying, pilling and calcining the composite. Chloroplatinic acid-ammonium hydroxide solution was added to the pills to form a final catalyst containing 0.3% platinum, following which the catalyst was calcined at a temperature of 932° F. for 3 hours.

Catalyst No. 4 was prepared in substantially the same manner as catalyst No. 3 except that subsequent to the addition of the chloroplatinic acids, magnesium nitrate was added in an amount to form a final catalyst containing 0.1% magnesium oxide and the catalyst then was calcined in the same manner as catalyst No. 3.

These catalysts were separately used for the reforming of a Mid-Continent naphtha having a boiling range of 182° F. to 402° F., a motor method octane number of 34.6, a research method octane number of 34.8, and a Reid vapor pressure of 1.0 pound. The reforming was effected at a temperature of 850° F. catalyst temperature, pressure of 500 pounds per square inch, a weight hourly space velocity of 2, and a hydrogen:hydrocarbon ratio of 3:1. Here again the runs were continued for 3 days. The results of the third day operation are shown in the following table:

Table II

	Catalyst No. 3	Catalyst No. 4
Yield, Weight Per Cent of Charge	92.7	94.1
Product:		
Octane Number, Motor Method	75.5	76.0
Octane Number, Research Method	83.6	80.8
Per Cent Aromatics	48.0	50.5
Carbon, Weight Per Cent of Catalyst	1.40	1.10

It will be noted that the catalyst containing magnesium oxide produced about 20% less carbon than was produced with a catalyst not containing magnesium.

From the data in Tables I and II, it is noted that the amount of carbon formed during the reforming operation is reduced. This reduction in carbon is very important from a commercial view point because it means that the process may continue for much longer periods of time before regeneration or replacement of the catalyst. This of course is important economically because it means that operation of the process does not have to be discontinued to regenerate or replace the catalyst as frequently as otherwise would be necessary and also the cost, both in manpower and equipment, of regenerating the catalyst is reduced.

I claim as my invention:

1. A conversion process which comprises subjecting a hydrocarbon to conversion in the presence of a catalyst comprising alumina, platinum, combined halogen and not more than about 1% by weight of an oxide of the group consisting of an alkaline earth metal and magnesium.

2. A conversion process which comprises subjecting a hydrocarbon to conversion in the presence of a catalyst comprising alumina, from about 0.01% to about 1% by weight of platinum, from about 0.1% to about 8% by weight of combined halogen and from about 0.01% to about 1% by weight of an oxide of the group consisting of an alkaline earth metal and magnesium.

3. A process for reforming a gasoline fraction which comprises subjecting said fraction to contact at reforming conditions with a catalyst comprising alumina, platinum, combined halogen and not more than about 1% by weight of calcium oxide.

4. A process for reforming a gasoline fraction which comprises subjecting said fraction to contact at reforming conditions with a catalyst comprising alumina, platinum, combined halogen and not more than about 1% by weight of magnesium oxide.

5. A process for the reforming of a gasoline fraction which comprises subjecting said fraction to reforming at reforming conditions in the presence of a catalyst comprising alumina, from about 0.01% to about 1% by weight of platinum, from about 0.1% to about 8% by weight of combined halogen and from about 0.01% to about 1% by weight of an oxide of the group consisting of an alkaline earth metal and magnesium.

6. The process of claim 5 further characterized in that said halogen comprises fluorine in an amount of from about 0.1% to about 3% by weight.

7. The process of claim 5 further characterized in that said halogen comprises chlorine in an amount of from about 0.2% to about 8% by weight.

8. The process of claim 5 further characterized in that said oxide comprises calcium oxide.

9. The process of claim 5 further characterized in that said oxide comprises magnesium oxide.

10. A method of preparing a catalyst which comprises combining a halogen with alumina, compositing platinum therewith, commingling an oxide of the group consisting of an alkaline earth metal and magnesium therewith in an amount not more than about 1% by weight of the composite, and calcining the composite.

11. A method of manufacturing a catalyst which comprises combining fluorine with alumi-

na in an amount of from about 0.1% to about 3% by weight of said alumina on a dry basis, thereafter commingling therewith platinum in an amount of from about 0.01% to about 1% by weight and calcium oxide in an amount of from about 0.01% to about 1% by weight, and calcining the resultant composite.

12. A method of manufacturing a catalyst which comprises combining fluorine with alumina in an amount of from about 0.1% to about 3% by weight of said alumina on a dry basis, thereafter commingling therewith platinum in an amount of from about 0.01% to about 1% by weight and magnesium oxide in an amount of from about 0.01% to about 1% by weight, and calcining the resultant composite.

13. A method of manufacturing a catalyst which comprises compositing fluorine with alumina in an amount of from about 0.1% to about 3% by weight of said alumina on a dry basis, drying said alumina-fluorine composite and forming the same into particles of uniform size and shape, thereafter commingling therewith platinum in an amount of from about 0.01% to about 1% by weight and calcium oxide in an amount of from about 0.01% to about 1% by weight, and calcining the resultant composite.

14. A method of manufacturing a catalyst which comprises compositing chlorine with alumina in an amount of from about 0.2% to about 8% by weight of said alumina on a dry basis, drying said alumina-chlorine composite and forming the same into particles of uniform size and shape, thereafter commingling therewith platinum in an amount of from about 0.01% to about 1% by weight and magnesium oxide in an amount of from about 0.01% to about 1% by weight, and calcining the resultant composite.

15. A catalyst comprising alumina, from about 0.01% to about 10% by weight of platinum, from about 0.1% to about 8% by weight of an oxide selected from the group consisting of the alkaline earth metal oxides and magnesia.

16. A catalyst comprising alumina, from about 0.01% to about 1% by weight of platinum, from about 0.1% to about 3% by weight of combined fluorine, and from about 0.01% to about 1% by weight of an oxide selected from the group consisting of the alkaline earth metal oxides and magnesia.

17. A catalyst comprising alumina, from about 0.01% to about 1% by weight of platinum, from about 0.1% to about 3% by weight of combined fluorine, and from about 0.01% to about 1% by weight of calcium oxide.

18. A catalyst comprising alumina, from about 0.01% to about 1% by weight of platinum, from about 0.1% to about 3% by weight of combined fluorine, and from about 0.01% to about 1% by weight of magnesium oxide.

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