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2,759,897

HYDROCARBON CONVERSION PROCESS AND CATALYST THEREFOR

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No Drawing. Application July 7, 1953,
Serial No. 366,625

11 Claims. (Cl. 252-442)

This invention relates to hydrocarbon conversion processes involving the treatment and conversion of hydrocarbons and to the manufacture of catalysts for use therein. It more specifically relates to a process for the reforming of gasoline in the presence of a catalyst that is calcined under selected conditions.

The term "reforming" is well-known in the petroleum industry and refers to the treatment of gasoline fractions to improve the antiknock characteristics thereof. The petroleum fraction that is up-graded in reforming may be a full boiling range straight run gasoline having an initial boiling point within the range of from about 50° F. to about 100° F. and an end boiling point within the range of from about 350° F. to about 425° F. It may also be a natural gasoline as obtained from the refining of natural gases or it may be any selected fraction of the natural gasoline. The natural gasoline or the natural gasoline fraction will have an initial boiling point and an end boiling point substantially the same as that of the gasoline hereinbefore described. In the reforming process the gasoline fraction that is selected usually is the higher boiling fraction, commonly referred to as naphtha and generally will have an initial boiling point of from about 150° F. to about 250° F. and an end boiling point within the range of from about 350° F. to about 425° F. The catalyst of the present invention may also be applied to the reforming of cracked gasoline or mixtures of cracked and straight run and/or natural gasoline. Reference to gasoline in the present specification therefore means a full boiling range gasoline or any fraction thereof and also that the gasoline fraction may contain components boiling above the gasoline range.

In the reforming process there are four major reactions. The first is an aromatization reaction in which naphthene hydrocarbons are converted to aromatics. The second is a dehydrocyclization reaction in which the straight chain or slightly branched chain paraffins are cyclicized to form aromatics. Third is an isomerization reaction in which straight chain or slightly branched chain paraffins are converted to more branched chain paraffins. This reaction occurs as a result of a strain put upon a carbon to carbon bond so that there is a shift of a carbon atom in the molecule to form a more branched chain molecule. In this specific reaction there is no change of molecular weight. The reaction may also be characterized as increasing the number of methyl groups in the hydrocarbon molecule. The fourth is a cracking reaction in which the heavier straight chain or slightly branched chain paraffins, which have low antiknock characteristics, are converted to lighter straight chain or branched chain paraffins, which have higher antiknock characteristics. When this last reaction is conducted in the presence of hydrogen the unsaturated hydrocarbon, which is formed as a result of the cracking operation, is saturated to the paraffin by reaction with hydrogen in the presence of the reforming catalyst. The cracking or splitting of the carbon to carbon bond is

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one of the more important reactions in a successful reforming process. It is necessary that the splitting of the carbon to carbon bond be controlled so that there is no unnecessary formation of normally gaseous products. For example, it would be possible to crack a C₁₀ hydrocarbon to form ten molecules of methane, however, unless methane is the specifically desired product, it would be uneconomical in a reforming process to crack the C₁₀ hydrocarbon to form methane. It is more desirable to crack a C₁₀ hydrocarbon so that two molecules of pentane are formed and it would be still more desirable if during the reaction isomerization would simultaneously take place so that the product obtained would be isopentane. It is an object of the present invention to provide a catalyst wherein the cracking activity is controlled and selective so that excessive amounts of normally gaseous products are not produced in a reforming process.

Uncontrolled or non-selective cracking results in the more rapid formation of larger quantities of coke or carbonaceous matter which deposits on the catalyst and decreases or destroys its activity to catalyze the desired reactions. This in turn results in shorter processing cycles or periods with the necessity of more frequent regeneration of the catalyst by burning the carbonaceous products therefrom, or should the catalyst activity be destroyed it will be necessary to shut-down the unit to remove the old catalyst and replace it with new catalyst.

Another important feature in a successful reforming process is the matter of hydrogen production and consumption. Investigation has shown that the presence of hydrogen in the reforming zone further tends to decrease the amount of carbonaceous deposit on the catalyst. In view of the fact that the cost of hydrogen is quite high, it is essential that there be no net consumption of hydrogen or, in other words, at least as much hydrogen must be produced in the process as is consumed therein.

While the catalyst of the present invention is particularly suitable for the reforming of gasoline, it is understood that this novel catalyst may be utilized for the conversion of other hydrocarbon fractions. Thus the catalyst may be used for the dehydrogenation of selected hydrocarbon fractions such as naphthenes to produce aromatics including specifically the dehydrogenation of cyclohexane to benzene, methylcyclohexane to toluene, ethylcyclohexane to ethylbenzenes, etc., the dehydrogenation of paraffins to produce the corresponding olefins, including specifically dehydrogenation of butane to butene, pentane to pentene, hexane to hexene, etc., the dehydrogenation of mono-olefins to produce the corresponding diolefins including specifically dehydrogenation of butene to butadiene, pentene to pentadiene, etc. The catalyst may also be utilized to effect dehydrocyclization reactions including specifically the conversion of normal hexane to benzene, normal heptane to toluene, etc. The catalyst may also be used for effecting isomerization reactions including the isomerization of normal or mildly branched chain paraffins, the isomerization of alkyl cyclic compounds to isomers thereof, including the isomerization of methylcyclopentane to cyclohexane, ethylcyclopentane to methylcyclohexane etc., the isomerization of alkyl benzenes, etc. Furthermore, the catalyst may be used for effecting hydrogenation reactions including non-destructive hydrogenation, as for example, the hydrogenation of octenes to octane, aromatics to cycloparaffins, etc., and destructive hydrogenation of heavier oil to gases and/or gasoline fractions. In still another embodiment the catalyst of the present invention may be used for effecting oxidation of hydrocarbons to form the corresponding oxides and alcohols, such as the oxidation of ethylene to ethylene oxide or butane to normal butyl alcohol.

The catalysts are also very effective for desulfurizing sulfur-containing fractions. The desulfurization may be effected in the presence or absence of hydrogen. In the desulfurization reaction the organic sulfur compounds such as mercaptans or thiophenes are converted to hydrogen sulfide which may be stripped out in subsequent operations.

In one embodiment the present invention relates to a conversion process which comprises subjecting a hydrocarbon to contact at conversion conditions with a catalyst prepared by commingling a solution of a platinum compound with alumina in an amount to form a final catalyst containing from about 0.01% to about 10% by weight of platinum, adding water to an oxygen-containing gas in an amount so that the oxygen-containing gas contains at least 0.01578 pound of water per pound of dry gas, and calcining the alumina-platinum composite in said gas containing the added water at a temperature of from about 700° F. to about 1100° F.

In another embodiment the present invention relates to a process for reforming a gasoline fraction which comprises subjecting said fraction to contact at a temperature of from about 500° F. 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 about 20 in the presence of from about 0.5 to about 20 mols of hydrogen per mol of hydrocarbon with a catalyst prepared by precipitating alumina from aluminum chloride, washing to remove chloride ions to below about 0.1% by weight of said alumina, combining a halogen with the alumina in an amount of from about 0.1% to about 8% by weight of said alumina on a dry basis, commingling a platinum-containing solution with the alumina containing halogen, adding water to an oxygen-containing gas in an amount to that the oxygen-containing gas contains at least 0.01578 pound of water per pound of dry gas, and calcining the alumina-platinum composite in said gas containing the added water at a temperature of from about 700° F. to about 1100° F.

In a further embodiment the present invention relates to a method of manufacturing a catalyst which comprises commingling a solution of a platinum compound with alumina in an amount to form a final catalyst containing from about 0.01% to about 10% by weight of platinum, adding water to an oxygen-containing gas in an amount so that the oxygen-containing gas contains at least 0.01578 pound of water per pound of dry gas, and calcining the alumina-platinum composite in said gas containing the added water at a temperature from about 700° F. to about 1100° F.

In a specific embodiment the present invention relates to a method of preparing a catalyst which comprises combining a halogen with alumina in an amount of from about 0.1% to about 8% by weight of said alumina on a dry basis, calcining the alumina-halogen composite at a temperature of from about 1000° F. to about 1400° F., commingling with the calcined particles a solution of a platinum compound in an amount to form a final catalyst containing from about 0.01% to about 10% by weight of platinum, adding water to an oxygen-containing gas in an amount so that the oxygen-containing gas contains at least 0.01578 pound of water per pound of dry gas, and calcining the alumina-platinum-halogen composite in said gas containing the added water at a temperature of from about 700° F. to about 1100° F.

The use of platinum as a catalyst for conversion processes has been of limited commercial acceptance because of the high cost of the catalyst. The present invention is based on the discovery that exceptionally good catalysts may be prepared to contain very low concentrations of platinum. While these catalysts may contain larger quantities of platinum, which may range up to about 10% by weight or more of the alumina, it has been found that exceptionally good catalysts may be prepared to contain as low as from about 0.01% to about 1% by

weight of platinum. Catalysts of these low platinum concentrations are particularly preferred in the present invention because of the considerably lower cost of the catalyst. It is well-known that platinum is very expensive and any satisfactory method of reducing the amount of platinum considerably reduces the cost of the catalyst and thus enhances the attractiveness of the catalyst for use in commercial processes.

However, in order to obtain improved results with these low platinum concentrations, it is necessary that a particular type of supporting component must be composited with the platinum. It has been found that alumina shows unexpected advantages for use as a supporting component for the low platinum concentrations apparently due to some peculiar association of the alumina with the platinum, either as a chemical combination or as a physical association. It has been found that the specific combination of alumina and low platinum concentration, not only is a very active catalyst, but also has a long catalyst life that is the catalyst retains its high activity for long periods of service. After these long periods of service the catalyst may show a drop in activity and it has further been found that the particular combination of alumina and platinum renders the catalyst susceptible to ready regeneration. Platinum on other supports such as alumina-silica, alumina-titania, and alumina-boron oxide also shows catalytic activity and the method of our invention for compositing platinum with alumina may also be used for compositing platinum with these other alumina-containing components but not necessarily with equivalent results.

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

To further improve these catalysts, it is a preferred feature of the present invention that the final catalyst contains halogen ions in a specific concentration. It has been found that the presence of halogen ions within a specific range effects a considerable improvement in the catalyst. It is believed that the halogen enters into some chemical combination or loose complex with the alumina and/or platinum and thereby seems to improve the final catalyst.

While any of the halogen ions will serve to effect improved results fluoride ions are particularly preferred. Next in order are the chloride ions, while the bromide and iodide ions are generally less preferred. Mixtures of the halogens may also be used and their concentrations will lie within the ranges hereinafter specified. It is understood that while any of the halogens will serve to effect an improvement they are not necessarily equivalent.

It is an essential feature of the present invention that the final composite of alumina-platinum compound, either with or without combined halogen, be calcined in an oxygen-containing atmosphere to which water has been added. As hereinbefore mentioned, the platinum appears to enter into some sort of a physical association or chemical combination with the alumina. When the platinum-alumina composite is calcined in air in which the water content is below a certain level it has been noted that the platinum has not completely associated itself with the

alumina. This is evidenced by the fact that platinum may be removed from an alumina-platinum composite after calcination in air by washing with a hot ammonium nitrate solution. This observation is important because it appears that the effectiveness of the catalyst is directly proportional to the amount of platinum that is intimately associated with the alumina. We have discovered that when water is added to an oxygen-containing gas and this gas is subsequently utilized as the atmosphere in which an alumina-platinum composite is calcined, the final catalyst resulting from this calcination appears to have the platinum more closely associated with the alumina. This is evidenced by the fact that upon repeated washings with hot ammonium nitrate solution the amount of platinum that is washed off the catalyst is substantially less than where the catalyst was calcined in air lacking a certain moisture content. We have discovered that when water is added to an oxygen-containing gas in an amount so that the oxygen-containing gas contains at least 0.01578 pound of water per pound of dry gas the resultant gaseous mixture is a superior calcining atmosphere than oxygen-containing gases containing lesser amounts of water. This is an unexpected result since previously it was believed that the primary purpose of the calcination step was to remove water from the catalyst and thus activate the catalytic components.

The amount of water that will saturate air at 70° F. seems to be satisfactory and the beneficial effect increases rapidly and the preferred lower temperature limit to measure the water content of the air is 100° F. Larger amounts of water or water vapor may be used within the scope of this invention with the amounts ranging from the amount necessary to saturate the calcining gas at 70° F. and preferably 100° F., to the amount of water vapor the calcining gas may hold at the calcination temperature. At 70° F. one pound of dry air is saturated by 0.01578 pound of water and at 100° F. one pound of dry air is saturated by 0.04305 pound of water. The temperature at which the final composite of alumina-platinum compound is calcined is usually within the range of from about 700° F. to about 1100° F. and the calcination is effected for a period of from about 2 to 12 hours or more.

In a preferred embodiment of the invention the alumina is formed into particles of uniform size and shape prior to the impregnation with the platinum compound. As another particular feature of this embodiment the alumina particles of uniform size and shape are subjected to calcination at a temperature above 1000° F. and preferably within the range of from about 1000° F. to about 1400° F. for a period of one to eight hours or more. The temperature and time of heating are correlated, that is, shorter times are employed with higher temperatures and longer times are employed with lower temperatures. On the other hand, the final composite containing platinum compound must not be heated at a temperature above 1100° F. and preferably is calcined in air to which water has been added in an amount so that air contains at least 0.04305 pound of water per pound of dry air, at a temperature of from about 700° F. to about 1100° F. for a period of 2 to 12 hours or more as hereinbefore set forth.

The catalyst of the present invention may be prepared in any suitable manner. A particularly preferred method is to prepare alumina 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 the aluminum salt, not only for con-

venience 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 washwater includes a small amount of ammonium hydroxide. The severity of washing will depend upon the particular method employed in preparing the catalyst. In one embodiment of the invention the alumina is thoroughly washed with a suitable amount of water and preferably water containing ammonium hydroxide to reduce the chlorine content of the alumina to below about 0.1%. In another embodiment of the invention this washing may be selective to retain chloride ions in an amount of from about 0.2% to about 8% by weight of the alumina on a dry basis. 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 chlorine is obtained in this manner.

In some cases it is desirable to prepare the catalyst in the form of pills of uniform size and shape and this may readily be accomplished by grinding the partially dried alumina cake with a suitable lubricant such as stearic acid, rosin, graphite, etc. and then forming the pills in any suitable pelleting or extrusion apparatus. The halogen may be added before or after forming the alumina into particles of uniform size and shape. In still another embodiment the halogen and platinum addition may be effected prior to forming the composite into particles of uniform size and shape. Alumina spheres may be continuously prepared by passing droplets of an alumina sol into an oil bath maintained at an elevated temperature and retaining the droplets in said oil bath until the droplets set to gel spheres. The spheres are continuously withdrawn from the oil bath and immediately thereafter aged prior to being contacted with water or aqueous solutions and subsequently dried and calcined at a temperature of from about 500° F. to 1400° F. or more.

Regardless of the stage of catalyst preparation at which the halogen is added the halogen may be incorporated therein in any suitable manner. However, the halogen must be added in a form which will readily react with the alumina in order to obtain the desired results and also must not leave undesired deposits in the catalyst. A preferred method of adding the halogen is in the form of an acid such as hydrogen fluoride, hydrogen chloride, hydrogen bromide and/or hydrogen iodide. Hydrogen fluoride is preferably added as an aqueous solution for ease in handling and for control of the specific amount to be added. Another satisfactory source to be used for adding the halogen is the volatile salts, such as ammonium fluoride, ammonium chloride, etc. The ammonium ions will be removed during the subsequent heating of the catalyst and, therefore, will not leave undesirable deposits in the catalyst. In still another method the halogen may be added as fluorine, chlorine, bromine or iodine, but in view of the fact that the halogens are normally more difficult to handle it is generally preferred to utilize them in the form of a solution for ease in handling. In some cases, the inclusion of certain components will not be harmful but may be beneficial and in these cases the halogen may be added in the form of suitable salts.

The concentration of halogen ion in the finished catalyst will be within the range of from about 0.1% to about 8% by weight of the alumina on a dry basis. The fluoride ion appears to be more active and therefore will be used within the range of from about 0.1% to about 3% by weight of the alumina on a dry basis. It has been found that halogen concentrations below these lower limits do not give the desired improvement and, on the

other hand, concentrations of halogen above the upper limits adversely effect the selectivity of the catalyst thus catalyzing side reactions to an extent greater than desired.

As hereinbefore set forth, it is preferred that the platinum compound be incorporated in the alumina or alumina-halogen composite in the presence of ammonium hydroxide to obtain uniform distribution of the platinum throughout the catalyst mass. In accordance with the preferred embodiment of the invention the alumina or alumina-halogen particles are impregnated with a platinum compound-ammonium hydroxide solution in order to obtain even distribution of the platinum compound throughout the alumina.

In a preferred step an aqueous solution of chloroplatinic acid is commingled with ammonium hydroxide in proportions to form a mixture and a pH within the range of from about 5 to about 10 and preferably within the range of from about 8 to about 10. This mixture is then commingled with the calcined alumina-halogen pills in the preferred embodiment of the invention, as hereinbefore set forth.

Regardless of the method of compositing the platinum with the alumina it has been found that the association of the platinum with the alumina is more complete when the calcination is performed in accordance with our invention.

After the chloroplatinic acid solution has been incorporated in the alumina pills the composite is dried at a temperature of from about 200° F. to about 500° F. for a period of from about 2 to 24 hours or more. Water is added to an oxygen-containing gas which is usually air in an amount so that the oxygen-containing gas contains at least 0.01578 pound of water per pound of dry gas, and the composite is then calcined in this gaseous mixture at a temperature of from about 700° F. to about 1100° F.

The humidification or adding of water may be performed in any suitable apparatus. The water addition may be done by indirect or direct humidifiers. The indirect humidifier usually comprises a chamber through which the air is drawn and inside the chamber are placed one or more banks of spray nozzles distributed uniformly over the cross-section area of the chamber. These nozzles are fitted with special spray tips which create a finely divided spray through centrifugal action. The direct humidifier usually comprises a spray nozzle type or atomizer head which is operated by the compressed air and the water is drawn into the nozzle by the current of compressed air. The spray nozzle in turn sprays water into an enclosed chamber through which the air, to which the water is to be added, is passing. The water may be added more directly by adding steam to the air before it is passed into the calcination zone or steam may be added directly into the calcination zone.

In the specification and claims the reference to water means water in the broad sense of the chemical formula H_2O and it may be in the liquid form or the gaseous form.

Although the catalyst of the present invention will have a long life it may be necessary to regenerate the catalyst after long periods of service. The regeneration may be effected by treatment with air or other oxygen-containing gas to burn the carbonaceous matter therefrom. In general, it is preferred to control the regeneration temperature not to exceed about 1100° F.

As hereinbefore set forth, these catalysts are particularly suitable for use in the reforming of gasoline or fractions thereof. The exact operating conditions depend upon the character of the charging stock, as well as the activity of the catalyst being used, however, the conditions usually will be in the following ranges: Temperatures from about 500° F. to about 1000° F., a pressure from about 50 to about 1000 p. s. i. or more, weight hourly space velocity (defined as the weight of oil per hour per weight of catalyst in the reaction zone) of from

about 0.5 to about 20 or more. The reforming is preferably effected in the presence of hydrogen which may be introduced from an extraneous source or recycled from within the process. In one embodiment of the process sufficient hydrogen will be produced in the reforming reaction to furnish the hydrogen required in the process and, therefore, it may be unnecessary to either introduce hydrogen from an extraneous source or to recycle hydrogen within the process. However, it usually will be preferred to introduce hydrogen from an extraneous source generally at the beginning of the operation and to recycle hydrogen within the process in order to be assured of a sufficient hydrogen atmosphere in the reaction zone. The hydrogen present in the reaction zone will be within the range of from about 0.5 to about 20 mols of hydrogen per mol of hydrocarbon. In some cases the gas to be recycled will contain hydrogen sulfide introduced with the charge or liberated from the catalyst and it is within the scope of the present invention to treat the hydrogen-containing gas to remove hydrogen sulfide or other impurities before recycling the hydrogen within the process.

Processes using the catalyst of the present invention may be effected in any suitable equipment. The finished catalyst may be deposited as a fixed bed in a reactor and the hydrocarbons to be treated are passed there-through in either upward or downward flow. The catalyst may be used in a fluidized type of operation in which the catalyst and hydrocarbons are maintained in a state of turbulence under hindered settling conditions, or a fluidized-fixed bed type of operation may be used in which the catalyst and hydrocarbons are maintained in a state of turbulence under hindered settling conditions but where catalyst is not withdrawn from or introduced into the reaction zone during the processing cycle. The catalyst may also be used in the moving bed type of process in which the catalyst and hydrocarbons are passed either in concurrent or countercurrent flow through a reaction zone, and the catalyst may also be used in the suspensoid type of operation in which the catalyst and hydrocarbons are passed as a slurry through the reaction zone. The reactants from any of the hereinbefore mentioned reaction zones are normally subjected to a further treatment, such as the stabilization of the product to separate normally gaseous paraffins therefrom to obtain a final reformed product of the desired volatility and vapor pressure.

The following examples are given to further illustrate the novelty and utility of the present invention, but are not given for the purpose of unduly limiting the generally broad scope of the present invention.

Example I

A catalyst was prepared in accordance with the present invention by adding ammonium hydroxide to aluminum chloride hexahydrate to form aluminum hydroxide. The resultant aluminum hydroxide was washed very thoroughly in order to reduce the chloride content to below 0.1% by weight on a dry basis. This washing entailed 6 separate washes with large amount of water containing a small amount of ammonium hydroxide and a final wash with water, with intervening filtering between the washes. An aqueous solution of hydrogen fluoride was added to the washed alumina in an amount of about 0.3% by weight of alumina on a dry basis. The alumina-fluorine composite was dried at a temperature of about 340° F. for 8-10 hours in order to reduce the moisture content to about 30%. The partially dried alumina was ground, Sterotex added as a lubricant, and then pilled in a Stokes pelleting machine to form cylindrical pills of $\frac{1}{8}$ " x $\frac{1}{8}$ " in size. The pills were then calcined in air at a temperature of about 932° F. for 6 hours to remove the lubricant and then further calcined at a temperature of about 1200° F. for 3 hours. Concentrated ammonium hydroxide solution (30%) was

added to a dilute solution of chloroplatinic acid (0.1 gram of chloroplatinic acid in 10 cc. of water). This solution produced no precipitate and had a pH of about 9. The solution was heated to boiling. The alumina pills were then soaked in this solution, the quantities being controlled to form a final catalyst containing 0.66% by weight of platinum. The mixture was then heated on a steam bath, after which the catalyst was dried at 230° F. for three hours. The catalyst sample was then divided into four equal portions of about 10 grams each. These equal portions are designated as A, B, C and D. Catalyst A was calcined in air at 482° F. for 3 hours. Catalyst C was also calcined in air at 482° F. for 3 hours but prior to the calcination the air was saturated with water at 80° F. so that the air contained 0.02226 pounds of water per pound of dry air. Catalyst B was calcined in air at 617° F. for 3 hours and catalyst D was calcined in air at 617° F. for 3 hours but prior to the calcination the air was saturated with water at 80° F. so that the air contained 0.02226 pound of water per pound of dry air. These catalysts were then washed with hot 5% ammonium nitrate solutions to remove the chloride brought in with the chloroplatinic acid and then they were finally washed with water. The samples were each washed six times with 210 ml. of the hot ammonium nitrate solution (203° F.-212° F.) and then water washed with approximately 100 ml. of water each. The samples were then dried and calcined at 932° F. for 3 hours. The samples were then checked for the platinum concentrations which were analyzed to be as follows:

A	B	C	D
0.260%	0.521%	0.568%	0.608%

The percentages are the percent by weight of platinum of the final catalyst.

It may easily be seen that the addition of water to the air produced a catalyst in which the platinum is more intimately associated with the alumina.

We claim as our invention:

1. A method of manufacturing a catalyst which comprises commingling a solution of a platinum compound with alumina in an amount to form a final catalyst containing from about 0.01% to about 10% by weight of platinum, adding water to air in an amount so that the air contains at least 0.01578 pound of water per pound of dry air, and calcining the alumina-platinum composite in said air containing the added water at a temperature of from about 700° F. to about 1100° F.

2. A method of manufacturing a catalyst which comprises commingling ammonium hydroxide and a platinum-containing solution with calcined particles of alumina, said solution being in an amount to form a final catalyst containing from about 0.01% to about 10% by weight of platinum, subsequently commingling with the alumina a halogen-containing solution in an amount to combine from about 0.1% to about 8% by weight of halogen with the alumina on a dry basis, adding water to air in an amount so that the air contains at least 0.01578 pound of water per pound of dry air and calcining the alumina-platinum-halogen composite in said air containing the added water at a temperature of from about 700° F. to about 1100° F.

3. The method of claim 2 further characterized in that

said halogen comprises fluorine in an amount of from about 0.1% to about 3% by weight of the alumina on a dry basis.

4. The method of claim 2 further characterized in that said halogen comprises chlorine in an amount of from about 0.2% to about 5% by weight of the alumina on a dry basis.

5. A method of manufacturing a catalyst which comprises combining a halogen with alumina in an amount of from about 0.1% to about 8% by weight of said alumina on a dry basis, calcining the alumina-halogen composite at a temperature of from about 1000° F. to about 1400° F., commingling with the calcined particles a solution of a platinum compound in an amount to form a final catalyst containing from about 0.01% to about 10% by weight of platinum, adding water to air in an amount so that the air contains at least 0.01578 pound of water per pound of dry air, and calcining the alumina-platinum-halogen composite in said air containing the added water at a temperature of from about 700° F. to about 1100° F.

6. The method of claim 5 further characterized in that said halogen comprises fluorine in an amount of from about 0.1% to about 3% by weight of the alumina on a dry basis.

7. The method of claim 5 further characterized in that said halogen comprises chlorine in an amount of from about 0.2% to about 5% by weight of the alumina on a dry basis.

8. A method of manufacturing a catalyst which comprises commingling alumina with a solution of a platinum compound and ammonium hydroxide in an amount to form a final catalyst containing from about 0.01% to about 10% by weight of platinum, adding water to air in an amount so that the air contains at least 0.01578 pound of water per pound of dry air and calcining the alumina-platinum composite in said air containing the added water at a temperature of from about 700° F. to about 1100° F.

9. A method of preparing a catalyst which comprises precipitating alumina from aluminum chloride, washing to remove chloride ions to below about 0.1% by weight of said alumina, combining a halogen with the alumina in an amount of from about 0.1% to about 8% by weight of said alumina on a dry basis, commingling a platinum-containing solution with the halogen-containing alumina, adding water to air in an amount so that the air contains at least 0.01578 pound of water per pound of dry air, and calcining the alumina-platinum composite in said air containing the added water at a temperature of from about 700° F. to about 1100° F.

10. In the preparation of platinized alumina catalyst, the improvement which comprises calcining alumina containing a platinum compound at a temperature of from about 700° F. to about 1100° F. in air containing at least 0.01578 pound of H₂O per pound of dry air.

11. In the calcining of alumina containing a platinum compound in air at a temperature of from about 700° F. to about 1100° F., the improvement which comprises adding H₂O to the air in an amount to provide therein at least 0.01578 pound H₂O per pound of dry air.

References Cited in the file of this patent

UNITED STATES PATENTS

2,479,110 Haensel ----- Aug. 16, 1949