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REFORMING PROCESS USING A GROUP VI METAL SULFIDE OR OXIDE-CONTAINING CATALYST

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This application is a continuation-in-part of my copending application Serial No. 259,319, filed November 30, 1951, now abandoned, which in turn is a continuation-in-part of my copending application Serial No. 142,931, filed February 7, 1950, now abandoned.

In the reforming process, gasoline is subjected to conversion to improve the anti-knock characteristics thereof. The gasoline may be substantially saturated and thus may comprise straight-run gasoline, natural gasoline, etc., or it may be an unsaturated gasoline, such as thermally cracked gasoline, or mixtures of saturated and unsaturated gasolines. The gasoline may be a full boiling range gasoline or any selected fraction thereof, the latter generally being referred to as naphtha. Reference to gasoline in the present specification and claims, therefore, is intended to mean a full boiling range gasoline or any fraction thereof.

The principal reactions in the reforming operation comprise dehydrogenation of six-membered ring naphthenic hydrocarbons to form aromatics, conversion of five-membered rings containing alkyl side chain or chains to aromatics, cyclization of straight chain or slightly branched chain aliphatic hydrocarbons to form aromatics, isomerization of straight chain or slightly branched chain aliphatic hydrocarbons to more highly branched chain structure, hydrogen transfer reactions, alkyl transfer reactions, controlled cracking or splitting of carbon to carbon bonds, etc.

In a successful reforming process the reactions, as hereinbefore set forth, are balanced in order to obtain a high yield of superior quality reformed gasoline. Particularly, the cracking must be controlled both in quantity and in quality, as a definite but small amount of cracking is advantageous in producing a reformate of higher volatility and of higher octane number and also in converting components in the charging stock boiling above the gasoline range, when present, into components within the gasoline range and, therefore, in further increasing the yield of desired gasoline. However, the cracking must not be excessive because it will result in the production of excessive amounts of normally gaseous products which cannot be used in the gasoline and, therefore, represent a loss of gasoline. Also excessive cracking results in increased deposition of carbon on the catalyst, and this carbon not only represents a loss of material which otherwise would go to gasoline, but also serves to deactivate the catalyst.

In one embodiment the present invention relates to a reforming process which comprises subjecting gasoline to contact at reforming conditions with a catalyst comprising alumina, halogen and a compound of a metal selected from the metals in the left hand column of group VI of the periodic table.

In a specific embodiment the present invention relates to a reforming process which comprises subjecting a gasoline fraction to contact at a temperature of from about 700° F. to about 1100° F. with a catalyst comprising alumina, from about 0.1% to about 10% by weight of

combined halogen, and from about 1% to about 20% by weight of tungsten trisulfide.

As hereinbefore set forth, in a reforming process, the desired primary reactions comprise dehydrogenation, isomerization and controlled cracking, and these reactions must be carefully balanced for successful operation. While various catalyst composites, including those of alumina-chromia, alumina-molybdena, etc., have been utilized heretofore in reforming operations, these catalysts are not entirely satisfactory in that they may be deficient in dehydrogenation, isomerization and/or selected cracking properties. These disadvantages are overcome by the novel catalyst of the present invention which, due to the peculiar influence of one component on the others, results in a catalyst which more properly effects the desired balance in these reactions. For example, the halogen, in combination with the other components, appears to modify the other components of the catalyst in effecting the desired isomerization and selected cracking reactions along with dehydrogenation.

A further advantage to the novel catalyst of the present invention is that these reactions may be effected at a lower temperature and this offers the further advantage of better control of the cracking reactions. For example, with the prior catalysts, it had been necessary to utilize higher temperatures in order to obtain cracking reactions and, when the higher temperatures were used, the cracking reactions occurred in excess. This resulted in a loss of charging stock to undesirable gaseous products, as well as in an increase in carbon deposits on the catalyst which, in turn, resulted in more rapid deactivation of the catalyst and consequently more frequent regeneration or replacement.

A primary component of the novel catalyst of the present invention comprises alumina. The alumina usually is present in a major proportion. Alumina appears to exert a peculiar beneficial influence on the other components of the catalyst and thereby results in a catalyst having unexpectedly improved properties for use in the reforming of gasoline.

Another component to be composited in the catalyst comprises a halogen, including fluorine, chlorine, iodine, and bromine. The preferred halogens comprise fluorine and chlorine. In general, fluorine appears to be less easily removed from the catalyst composite and of higher activity and, therefore, is preferred in many cases. It is understood that the halogen may comprise a mixture of two or more of the halogens, a preferred mixture comprising fluorine and chlorine.

The next component in the catalyst comprises a compound and particularly an oxide or sulfide of a metal selected from the metals in the left hand column of group VI of the periodic table, and specifically a sulfide of moylbdenum, chromium, tungsten, and/or uranium. Of these the sulfide of tungsten is particularly preferred. However, it is understood that two or more of these sulfides may be used in the catalyst although not necessarily with equivalent results.

The charge stocks that may be reformed in accordance with my process comprise hydrocarbon fractions that boil within the gasoline range and that contain aromatics and paraffins. The preferred stocks are those consisting predominantly of aromatics, naphthenes, and paraffins, although minor amounts of olefins may be present. This preferred class includes straight-run gasoline, natural gasoline and the like. The gasoline fraction may be a full boiling range 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 300° F. to about 425° F., or it may be a selected fraction thereof which usually is a higher boiling fraction com-

monly referred to as naphtha and having an initial boiling point within the range 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. Mixtures of the various gasolines and/or gasoline fractions may also be used and thermally and/or catalytically cracked gasolines may also be used as charging stock, however, when these unsaturated gasoline fractions are used, it is preferred that they be used in admixture with a straight-run or natural gasoline fraction, or hydrogenated before use in the process.

In some cases it is desirable to reform the gasoline fraction so that a specific product of a narrow boiling range is formed. When it is desired to produce toluene, the hydrocarbon fraction is fractionated into what is referred to as a "pre-toluene" fraction, that is, a fraction which contains constituents which upon reforming form toluene. These toluene-forming constituents boil below the boiling point of toluene; therefore, the selected fraction is one boiling below toluene and the preferred boiling range is from about 150° F. to about 220° F. Many of the benzene-forming components are also in this selected fraction and, therefore, benzene may also be produced in the reforming process. Initial boiling points lower than this may be utilized; however, they do not usually contain enough of the aromatic-producing compounds and, therefore, the preferred initial boiling point is 150° F. and an end boiling point of 220° F. is preferred since the fraction boiling below 220° F. contains only slight amounts of naturally occurring toluene and, therefore, the maximum conversion to toluene is possible in the equilibrium reaction.

A higher boiling fraction, boiling within the range of from about 240° F. to about 285° F. may also be reformed. This higher boiling fraction is often called the "pre-xylene" fraction and contains ethylcyclohexane and dimethylcyclohexane components which are converted to xylenes and ethylbenzene in the reforming operation. It is also within the scope of this invention to mix the "pre-xylene" and "pre-toluene" fraction, that is the 150° F. to 220° F. fraction and the 240° F. to 285° F. fraction and then reform the mixture. Toluene is easily separated from the reformed mixture by fractional distillation.

The charge to the present reforming operation may also comprise a lower boiling fraction recovered from petroleum distillates and boiling within the range of from about 150° F. to about 185° F. Upon reforming, the methylcyclopentane and the cyclohexane in this fraction are converted to benzene and the benzene may be recovered by any suitable process such as fractional distillation, solvent extraction, etc.

The term "reforming" is well known in the petroleum industry and refers to the treatment of gasoline fractions to improve the anti-knock characteristics. The present invention is directed to the reforming of gasoline or gasoline fractions, the boiling ranges of several specific ones which were hereinabove mentioned.

In accordance with the present invention, the alumina will comprise a major proportion of the catalyst. The halogen generally will be used in amounts of from about 0.1% to about 10% by weight of the final catalyst. When fluorine is the halogen, it preferably will be used in amounts of from about 0.1% to about 5% by weight of a catalyst and when cholorine is the halogen it generally will be used in amounts of from about 0.2% to about 10% by weight of the catalyst. As hereinbefore set forth the halogen may comprise a mixture of two or more halogens and the total amount of halogen preferably is within the ranges herein set forth. The sulfide of the metal in Group VI of the Periodic Table preferably is utilized in an amount of from about 1% to about 20% by weight of the final catalyst although in some cases higher concentrations may be used.

The catalyst composite of the present invention may be prepared in any suitable manner including separate, successive or coprecipitation methods. In separate precipitation methods the alumina may be prepared in any suitable manner as, for example, by reacting a basic reagent such as ammonium hydroxide, ammonium carbonate, etc. with an acid salt solution of aluminum as, for example, the chloride, sulfate, nitrate, etc., or by adding an acid to an alkali salt of aluminum as, for example, commingling sulfuric acid with sodium aluminate, etc. Usually the alumina will be washed and filtered, which may be done in the same or separate steps and may be effected in the presence of an acid or base as desired. The wet slurry may be dried, formed into particles of uniform or irregular size and shape by suitable methods such as grinding, pelleting, extrusion, etc. and then may be calcined. In another embodiment, the alumina may be formed into substantially spherical gel particles in any suitable manner. The other component or components of the catalyst may then be composited with the preformed particles of alumina, either by conventional precipitation from a salt or by intimately mixing a naturally occurring oxide with the alumina, preferably in a wet state.

When successive precipitation methods are employed, the alumina is precipitated as hereinbefore set forth and then the wet slurry, either with or without prior washing, may be composited with a salt of the other component, and precipitation of the oxide is effected by the addition of a suitable base or acid as required. The composite may then be dried, formed into particles and calcined.

In coprecipitation methods, the alumina and oxide of the other component or components are precipitated simultaneously from suitable compounds, followed by washing, drying and calcining.

The halogen may be added to the catalyst in any suitable manner and either before or after precipitation of the oxides. While the halogen may be utilized as such, it generally is preferred to utilize the same as an aqueous solution of the hydrogen halide for ease in handling. In the preferred method, the halogen is added to the alumina before the final component is composited therewith.

The tungsten sulfide may be incorporated into the catalyst in any suitable method. In a preferred method a water soluble tungstate is dissolved in water and the alumina, before or after combining with the halogen, is impregnated with this aqueous solution of the water soluble tungstate. The tungstate may be converted to the sulfide by use of a suitable sulfiding agent such as ammonium sulfide, hydrogen sulfide, etc. In another method the alumina, before or after adding the halogen, is impregnated with an aqueous solution of a thiotungstate, specifically $(NH_4)_2WS_4$. The mixture is then acidified and the trisulfide, WS_3, is precipitated.

As hereinbefore set forth the catalyst or components thereof, in one method of manufacture, are dried, formed into particles of uniform size and shape and calcined. The drying generally will be effected at a temperature of from about 200° F. to about 500° F. for a period of from about two to twenty-four hours or more. Calcination generally is effected at a temperature of from about 500° F. to 1600° F. or more for a period of two to twelve hours or more. The calcination may be effected in the presence of air, a reducing atmosphere such as hydrogen, an inert atmosphere such as nitrogen, or a mixture thereof. In still another embodiment the catalyst may be calcined in a reducing atmosphere and then calcined in an oxidizing atmosphere, or the reverse procedure may be utilized.

As hereinbefore set forth, the components of the catalyst serve to exert a peculiar influence on each other, with the result that a more effective catalyst is obtained. The association of these components may be physical, chemical or a combination thereof. The exact state of the halogen and other components of the catalyst has not been established but the halogen undoubtedly is present

in a combined state, preferably in association with the alumina and/or other metal oxide.

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 deposit therefrom. In general, it is preferred to control the regeneration temperature not to exceed about 1200° F. In some cases it may be desirable to follow the burning operation with a treatment with hydrogen-containing gas at a temperature of from about 700° F. to about 1200° F.

As hereinbefore set forth, these catalysts are particularly suitable for use in the reforming of gasoline or fractions thereof. The reforming operation may be effected at a temperature within the range of from about 700° F. to about 1100° F. or more, a pressure within the range of from about 5 to 2000 pounds per square inch or more, and a weight hourly space velocity (defined as the weight of oil per hour per weight of catalyst in the reaction zone) of from about 0.1 to 20 or more. The reforming preferably is effected in the presence of hydrogen, which may be introduced from an extraneous source or recycled from within the process. In a preferred operation, sufficient hydrogen will be produced in the reforming operation to furnish the hydrogen required in the process and, therefore, it may be unnecessary to introduce hydrogen from an extraneous source. In general, the concentration of hydrogen in the reaction zone will be within the range of from about 0.5 to 20 mols or more of hydrogen per mol of hydrocarbon.

The process of the present invention may be effected in any suitable equipment. A particularly suitable process comprises the well known fixed bed system in which the catalyst is disposed in a reaction zone and the hydrocarbons to be treated are passed therethrough in either upward or downward flow. The products are fractionated to separate hydrogen and to recover the desired products. As hereinbefore set forth, the hydrogen is preferably recycled for further use 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 fluidized-fixed bed type process in which the reaction is effected in a manner similar to the fluidized type process but the catalyst is not withdrawn from the reaction zone as in the fluidized type process, the compact moving bed type in which the catalyst and hydrocarbons are passed either concurrently or countercurrently to each other, and the suspensoid type of operation in which the catalyst is carried into a reaction zone as a slurry in the hydrocarbon oil.

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

Example I

An alumina-fluorine-chromia catalyst was prepared to contain 8.3% chromia, 0.35% fluorine and the remainder alumina. Alumina was precipitated by adding ammonium hydroxide to a chloride of aluminum, and the resultant washed but undried alumina was slurried in sufficient water to make a rather thick slurry. Aqueous hydrogen fluoride solution in an amount to form a final catalyst containing 0.35% by weight of fluorine was added to the slurry with constant stirring. The resultant alumina-halogen mixture was dried for nine hours at 338° F., ground to pass through 40 mesh screen, a lubricant added and the composite formed into cylindrical pills. The pills were then treated with oxygen at an elevated temperature to burn out the lubricant, after which the pills were calcined for two hours at about 1200° F.

Chrome flakes (CrO_3) were dissolved in water and poured over the pills, after which the mixture was allowed to stand for ten minutes, the excess solution drained off and the pills then dried at about 300° F. for eighteen hours and finally calcined at 1022° F. for two hours. The solution of chrome flakes was utilized in an amount to form a final chromia (Cr_2O_3) concentration of 8.3% by weight.

A catalyst as prepared in the above manner was utilized for the reforming of a naphtha having an initial boiling point of 220° F., an end boiling point of 398° F., and a Research Method clear octane number of 30 which increased to 58.9 upon the addition of 3 cc. of tetraethyl lead per gallon. The reforming was effected at a catalyst temperature of about 950° F., a pressure of 500 pounds per square inch, a space velocity of 2 and in the presence of hydrogen in a mol ratio of hydrogen to hydrocarbon of 3.15:1. In this operation there was produced a debutanized reformate in a yield of 82.8% by volume of the charge, which reformate had a Research Method clear octane number of 76.2, which increased to 90 upon the addition of 3 cc. of tetraethyl lead. This catalyst was used for a total of forty-six hours in a pilot plant run and had a carbon content at the end of the run of only 0.7% by weight of the catalyst.

Example II

An alumina-chlorine-molybdenum oxide catalyst may be prepared to comprise 0.8% by weight of chlorine, 12% by weight of molybdenum oxide and the remainder alumina. This catalyst may be prepared by commingling an aqueous hydrogen chloride solution with precipitated alumina and then adding an ammonium molybdate solution to the wet mixture of alumina-halogen. The amounts of acid and ammonium molybdate solutions are regulated to form the final catalyst as hereinbefore set forth.

The catalyst as prepared in the above manner may be utilized for the reforming of a Mid-Continent gasoline at a temperature of 975° F., a pressure of 600 pounds per square inch in the presence of hydrogen in a mol ratio of hydrogen to hydrocarbon of 4:1.

Example III

A composite of alumina and fluorine may be prepared by adding ammonium hydroxide to aluminum chloride to form aluminum hydroxide, washing with ammoniated water to remove soluble impurities, commingling an aqueous hydrogen fluoride solution therewith in an amount to form a final catalyst containing 0.5% by weight of combined fluorine in the final catalyst, drying the composite at a temperature of 300° F., commingling graphite therewith and forming the composition into pills of uniform size and shape by a pelleting operation, and calcining the pills at a temperature of 1200° F. The calcined pills are then suspended in a solution of ammonium chromate, the amount of chromium compound being controlled to produce a final catalyst containing 12% by weight of chromia as Cr_2O_3.

This catalyst may be used for the reforming of a Mid-Continent gasoline at a temperature of 950° F. and a pressure of 800 pounds per square inch in the presence of hydrogen at a hydrogen to hydrocarbon mol ratio of 3:1.

Example IV

An alumina-fluorine-tungsten trisulfide catalyst is prepared to contain 0.5% fluorine, 7.5% by weight of tungsten trisulfide and the balance alumina. Alumina is precipitated by adding ammonium hydroxide to a chloride of aluminum, and the resultant washed but undried alumina is slurried in sufficient water to make a thick slurry. A hydrogen fluoride solution is added to the slurry in an amount to form a final catalyst containing 0.5% by weight of combined fluorine. The resultant alumina-fluorine mixture is dried for three hours at 500° F., ground, mixed with Sterotex as a lubricant and the composite formed into cylindrical pills in a pelleting machine. The pills are then calcined in air for three hours at about 1200 ° F.

An aqueous solution of ammonium thiotungstate, $(NH_4)_2WS_4$, is prepared and added to the pills in an amount to form a final catalyst containing 7.5% tungsten trisulfide. The solution is allowed to remain in contact with the pills for approximately one-half hour and hydrogen chloride is added to acidify the impregnating solution thereby converting the thiotungstate to tungsten trisulfide. The mixture is then evaporated to dryness and the catalyst heated in a hydrogen sulfide atmosphere at 500° F. for approximately three hours.

This catalyst may be used for the reforming of a gasoline under substantially the same conditions as described in Example I.

I claim as my invention:

1. A reforming process which comprises subjecting a gasoline fraction to contact at a reforming temperature of from about 700° F. to about 1100° F. with a catalyst consisting essentially of alumina, from 0.1% to about 10% by weight of combined halogen, and from about 1% to about 20% by weight of a compound selected from the group consisting of the sulfides and oxides of molybdenum, chromium and tungsten.

2. The process of claim 1 further characterized in that said compound is a sulfide.

3. A reforming process which comprises subjecting a gasoline fraction to contact at a reforming temperature of from about 700° F. to about 1100° F. with a catalyst consisting essentially alumina, from 0.1% to about 10% by weight of combined halogen, and from about 1% to about 20% by weight of tungsten sulfide.

4. A reforming process which comprises subjecting a gasoline fraction to contact at a reforming temperature of from about 700° F. to about 1100° F. with a catalyst consisting essentially of alumina, from about 0.2% to about 10% by weight of combined chlorine, and from about 1% to about 20% by weight of tungsten sulfide.

5. A reforming process which comprises subjecting a gasoline fraction to contact at a reforming temperature of from about 700° F. to about 1100° F. with a catalyst consisting essentially of alumina, from about 0.1% to about 5% by weight of combined fluorine, and from about 1% to about 20% by weight of tungsten sulfide.

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