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[54] **REFORMING OF HYDROCARBON FEED STOCKS WITH A CATALYST COMPRISING PLATINUM AND TIN**

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Related U.S. Application Data

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[52] **U.S. Cl.** **208/139,** 208/138

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[58] **Field of Search** 208/138, 139

[56] **References Cited**

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[57] **ABSTRACT**

A process for reforming a hydrocarbon feed stock which comprises heating said charge stock in contact with a catalytic composite comprising a tin component and a platinum component on a carrier material at reforming conditions including a pressure of from about 0 to about 1000 psig and a temperature of from about 800° to about 1,100° F. The catalytic composite is characterized by a method of preparation. A high surface area porous carrier material is impregnated with a solution comprising a trichlorostannate (II)-chloroplatinate anionic complex and thereafter dried and calcined to yield the catalytic composite.

9 Claims, No Drawings

REFORMING OF HYDROCARBON FEED STOCKS WITH A CATALYST COMPRISING PLATINUM AND TIN

RELATED APPLICATIONS

This application is a division of a copending application Ser. No. 102,059 filed Dec. 28, 1970, now U.S. Pat. No. 3,725,304.

The reforming of gasoline boiling range feed stocks to improve the octane rating thereof is a process well-known to the petroleum industry. The feed stock may be a full boiling range gasoline fraction boiling in the 50°–425°F. range, although it is more often what is commonly called naphtha — a gasoline fraction characterized by an initial boiling point of from about 150° to about 250° F. and an end boiling point of from about 350° to about 425° F.

The reforming of gasoline boiling range feed stocks is generally recognized as involving a number of octane-improving hydrocarbon conversion reactions requiring a multi-functional catalyst. In particular, the catalyst is designed to effect several octane-improving reactions with respect to paraffins and naphthenes — the feed stock components that offer the greatest potential for octane improvement. Thus, the catalyst is designed to effect isomerization, dehydrogenation, dehydrocyclization and hydrocracking of paraffins. Of these hydrocarbon conversion reactions, dehydrocyclization produces the greatest gain in octane value and is therefore a favored reaction. For naphthenes, the principal octane-improving reactions involve dehydrogenation and ring isomerization to yield aromatics of improved octane value. With most naphthenes being in the 65–80 F-1 clear octane range, the octane improvement, while substantial, is not as dramatic as in the case of the lower octane paraffins. Reforming operations thus employ a multi-functional catalyst designed to provide the most favorable balance between the aforementioned octane-improving reactions to yield a product of optimum octane value, said catalyst having at least one metallic dehydrogenation component and an acid-acting hydrocracking component.

However, even with the achievement of desired balance between the octane-improving reactions, problems persist relating principally to undesirable side reactions, which, although minimal, cumulatively contribute to carbon formation, catalyst instability and product loss. Thus, demethylation occurs with the formation of excess methane; excessive hydrocracking produces light gases; cleavage or ring opening of naphthenes results in the formation of low octane, straight-chain hydrocarbons; condensation of aromatics forms coke precursors and carbonaceous deposits; and the acid catalyzed polymerization of olefins and other polymerizable materials yields high molecular weight hydrocarbons subject to dehydrogenation and further formation of carbonaceous matter.

Accordingly, an effective reforming operation is dependent on the proper selection of catalyst and process variables to minimize the effect of undesirable side reactions for a particular hydrocarbon feed stock. However, the selection is complicated by the fact that there is an interrelation between reaction conditions relating to undesirable side reactions and desirable octane-improving reactions. Reaction conditions selected to optimize a particular octane-improving reaction may,

and often do, also promote one or more undesirable side reactions. For example, as previously indicated, some hydrocracking is desirable since it produces lower boiling hydrocarbons of higher octane value than the parent hydrocarbons. But hydrocracking of the lower boiling C_6–C_8 constituents is not desirable since it produces still lower boiling hydrocarbons, such as butane, which are of marginal utility. It is this type of hydrocracking that is referred to as excessive hydrocracking and to be avoided. The extent and kind of hydrocracking is controlled by careful regulation of the acid-acting component of the catalyst and by the use of low hydrogen partial pressures. The latter follows from the fact that the hydrocracking reaction consumes hydrogen and the reaction can therefore be controlled by limiting hydrogen concentration in the reaction media. Low hydrogen partial pressures have a further advantage in that the main octane-improving reactions, i.e., dehydrogenation of paraffins and naphthenes, are net producers of hydrogen and, as such, favored by low hydrogen pressures.

Catalysts comprising a supported platinum group metal, for example platinum supported on alumina, are widely known for their selectivity in the production of high octane aromatics, general activity with respect to each of the several octane-improving reactions which make up the reforming operation, and for their stability at reforming conditions. One of the principal objections to low pressure reforming relates to its effect on catalyst stability. This stems from the fact that low pressure operation tends to favor the aforementioned condensation and polymerization reactions believed to be the principal reactions involved in the formation of coke precursors and carbon deposits so detrimental to catalyst stability.

More recently, the industry has turned to certain multi-component or bi-metallic catalysts to make low pressure reforming, and all the advantages attendant therewith, a reality. While tin promoted platinum catalysts have been proposed, the activity, selectivity, and particularly the stability have not heretofore been adequate to warrant commercial acceptance on any appreciable scale.

It is generally recognized that catalysis involves a mechanism particularly noted for its unpredictability. Minor variations in a method of manufacture often result in an unexpected improvement in the catalyst product. The improvement may result from an undetermined and minor alteration of the physical character and/or composition of the catalyst product to yield a novel composition difficult of definition and apparent only as a result of substantially improved activity, selectivity and/or stability realized with respect to one or more conversion reactions. For example, it has been discovered that the aforementioned tin-promoted platinum catalysts, modified in the course of manufacture with respect to the method of impregnating the tin and platinum components on a carrier material, exhibits a substantial improvement over prior art tin-platinum reforming catalysts, particularly with respect to stability.

In one of its broad aspects, the present invention embodies a process for reforming a hydrocarbon feed stock which comprises heating said charge stock in contact with a catalytic composite at reforming conditions including a pressure of from about 0 to about 1000 psig and a temperature of from about 800° to

about 1,100° F., said catalytic composite consisting essentially of a tin component in combination with a platinum component on a carrier material and prepared by the method which comprises (a) impregnating a high surface area, porous carrier material with a solution of a complex chlorostannate (II)-chloroplatinate anionic species, said solution being stabilized in contact with said carrier material with an aqueous halogen acid, and (b) drying and calcining the impregnated carrier material.

Other objects and embodiments of this invention will become apparent in the following detailed specification.

In accordance with the present invention, a high surface area, porous carrier material is impregnated with a solution of a complex chlorostannate (II)-chloroplatinate anionic species. Catalysts such as herein contemplated typically comprise platinum although other platinum group metals including palladium, ruthenium, rhodium, iridium and osmium can be utilized. Also, such catalysts typically contain a halogen component, usually chlorine, although bromine, iodine and fluorine may be utilized. Thus, in one of the more preferred embodiments of this invention, the impregnating solution is prepared to contain a complex trichlorostannate (II)-chloroplatinate anionic species and, in the interest of clarity, the subsequent description of the invention is presented with respect thereto.

The chloroplatinate moiety of the preferred complex trichlorostannate (II)-chloroplatinate anionic species is intended to include the anionic hexachloroplatinate (IV) containing platinum in the +4 valence state, and also the anionic tetrachloroplatinate (II) containing platinum in the +2 valence state. In any case, the preferred complex anionic species further comprises the anionic trichlorostannate (II), substituted for one or more labile chlorine atoms of the aforementioned anionic chloroplatinate. For example, in the preferred complex anionic species, the trichlorostannate anion ($SnCl_3^-$) is substituted for one or more labile chlorine atoms of an anionic chloroplatinate (IV) to form said complex anionic species substantially in accordance with the anionic formulae $[PtCl_4(SnCl_3)_2]^{2-}$ and $[PtCl_5(SnCl_3)]^{2-}$. Correspondingly, the trichlorostannate anion is substituted for one or more labile chlorine atoms of the anionic chloroplatinate (II) to form a complex anionic species substantially in accordance with the anionic formulae $[PtCl_3(SnCl_3)]^{2-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$. In any case, the trichlorostannate (II) moiety of the complex anionic species contains tin in the +2 valence state.

The impregnating solution of this invention may be prepared by conventional methods disclosed in the art. For example, the preferred complex anionic species may be prepared substantially in accordance with the method of Young et al. (Journal of the Chemical Society, 1964, 5176). Thus, stannous chloride is reacted with sodium chloroplatinite (II) at about room temperature in dilute hydrochloric acid to yield a suitable complex tin-platinum anionic species. Preferably, the impregnating solution is prepared by commingling stannous chloride with chloroplatinic acid at about room temperature. The stannous chloride and chloroplatinic acid are suitably commingled in a mole ratio of from about 1:1 to about 10:1 although a mole ratio of from about 1:1 to about 2:1 is preferred.

In any case, the impregnating solution is acidified with an aqueous halogen acid, preferably aqueous hydrochloric acid, to stabilize the desired complex anionic species upon contact with the selected carrier material. The pH of the impregnating solution is suitably adjusted at less than about 3, and preferably less than about 1, prior to contact with the carrier material. The hydrochloric acid obviates instability of the complex anionic species upon contact with the carrier material, an instability believed to result from carrier adsorption of halogen from the complex anionic species, and thus preserves the intimate association of the tin and platinum components essential to the improved activity, selectivity and stability of the final catalyst product.

Pursant to the method of the present invention, a high surface area, porous carrier material is impregnated with the described complex anion species in solution. Suitable carrier materials include any of the various and well-known solid adsorbent materials generally utilized as a catalyst support or carrier. Said adsorbent materials include the various charcoals produced by the destructive distillation of wood, peat, lignite, nut shells, bones, and other carbonaceous matter, and preferably such charcoals as have been heat treated, or chemically treated, or both, to form a highly porous particle structure of increased adsorbent capacity, and generally defined as activated carbon. Said adsorbent materials also include the naturally occurring clays and silicates, for example, diatomaceous earth, fuller's earth, kieselguhr, Attapulgus clay, feldspar, montmorillonite, halloysite, kaolin and the like, and also the naturally occurring or synthetically prepared refractory inorganic oxides such as alumina, silica, zirconia, thoria, boria, etc., or combinations thereof like silica-alumina, silica-zirconia, alumina-zirconia, etc. The preferred porous carrier materials for use in the present invention are the refractory inorganic oxides with best results being obtained with an alumina carrier material. It is preferred to employ a porous, adsorptive, high surface area material characterized by a surface area of from about 25 to about 500 square meters per gram. Suitable aluminas thus include gamma-alumina, eta-alumina, and theta-alumina, with the first mentioned gamma-alumina being preferred. A particularly preferred alumina is gamma-alumina characterized by an apparent bulk density of from about 0.30 to about 0.70 grams per cubic centimeter, an average pore diameter of from about 50 to about 150 Angstroms, an average pore volume of from about 0.10 to about 1.0 cubic centimeters per gram, and a surface area of from about 150 to about 500 square meters per gram.

The alumina employed may be a naturally occurring alumina or it may be synthetically prepared in any conventional or otherwise convenient manner. The alumina is typically employed in a shape or form determinative of the shape or form of the final catalyst composition, e.g., spheres, pills, granules, extrudates, powder, etc. A particularly preferred form of alumina is the sphere, especially alumina spheres prepared substantially in accordance with the oil-drop method described in U.S. Pat. No. 2,620,314. Briefly, said method comprises dispersing droplets of an alumina sol in a hot oil bath. The droplets are retained in the oil bath until they set into firm gel spheroids. The spheroids are continuously separated from the bath and subjected to specific aging treatments to promote certain desirable properties. The spheres are subsequently dried at about from

105° to about 395° F. and thereafter calcined at from about 800° to about 1400° F.

Impregnating conditions employed herein involve conventional impregnating techniques known to the art. Thus, the catalytic components, or soluble compounds thereof, are adsorbed on the carrier material by soaking, dipping, suspending, or otherwise immersing the carrier material in the impregnating solution, suitably at ambient temperature conditions. The carrier material is preferably maintained in contact with the impregnating solution at ambient temperature conditions for a brief period, preferably for at least about 30 minutes, and the impregnating solution thereafter evaporated substantially to dryness at an elevated temperature. For example, a volume of alumina particles is immersed in a substantially equal volume of impregnating solution in a steam-jacketed rotary dryer and tumbled therein for a brief period at about room temperature. Thereafter, steam is applied to the jacket of the dryer to expedite the evaporation of said solution and recovery of substantially dry impregnated carrier material.

Catalysts such as herein contemplated typically are prepared to contain a halogen component which may be chlorine, fluorine, bromine and/or iodine. The halogen component is generally recognized as existing in a combined form resulting from physical and/or chemical combination with the carrier or other catalyst components. While at least a portion of the halogen component may be incorporated in the catalyst composition during preparation of the carrier material, sufficient halogen is contained in the aforesaid impregnating solution to enhance the acidic function of the catalyst product in the traditional manner. In any case, a final adjustment of the halogen level may be made in the manner hereinafter described.

In summary, one preferred embodiment of the impregnating step of the present invention utilizes an impregnating solution comprising a complex trichlorostannate (II)-chloroplatinate anion species prepared by commingling stannous chloride with chloroplatinic acid in about a 1:1 mole ratio, the impregnating solution being stabilized with aqueous hydrochloric acid at a pH of less than about 1. A concentration of tin and platinum group metal in the impregnating solution is selected to yield a final catalyst composite containing from about 0.01 to about 5.0 wt. percent tin and from about 0.01 to about 2.0 wt. percent platinum calculated on an elemental basis. Excellent results are obtained when the catalyst contains from about 0.05 to about 1.0 wt. percent each of tin and platinum.

Regardless of the details of how the components of the catalyst are combined with the porous carrier material, the final catalyst composite generally will be calcined in an oxidizing atmosphere such as air at a temperature of from about 400° to about 1200° F. The catalyst particles are advantageously calcined in stages to experience a minimum of breakage. Thus, the catalyst particles are advantageously calcined for a period of from about 1 to about 3 hours in an air atmosphere at a temperature of from about 400° to about 700° F., and immediately thereafter at a temperature of from about 900° to about 1,200° F. in an air atmosphere for a period of from about 3 to about 5 hours. Best results are generally obtained when the halogen content of the catalyst is adjusted during the calcination step by including a halogen or a halogen-containing compound in the air atmosphere utilized. In particular, when the halogen component of the catalyst is chlorine, it is preferred to use a mole ratio of H_2O to HCl of from about 20:1 to about 100:1 during at least a portion of the calcination step in order to adjust the final chlorine content of the catalyst to a range of from about 0.6 to about 1.2 wt. percent.

It is preferred that the resultant calcined catalytic composite is subjected to a substantially water-free reduction step prior to its use in the conversion of hydrocarbons. This step is designed to further insure a uniform and finely divided dispersion of the metallic components throughout the carrier material. Preferably, substantially pure and dry hydrogen (i.e., less than 20 volume ppm H_2O) is used as the reducing agent in this step. The reducing agent is contacted with the oxidized catalyst at conditions including a temperature of from about 800° to about 1,200° F. This reduction step may be performed in situ as part of a start-up sequence if precautions are taken to predry the plant to a substantially water-free state and if substantially water-free hydrogen is used. The duration of this step is preferably less than 2 hours, and more typically about 1 hour.

Reforming of gasoline feed stocks in contact with the catalyst of this invention as herein contemplated, is suitably effected at a pressure of from about 0 to about 1000 psig and at a temperature of from about 800° to about 1100° F. The catalyst of this invention permits a stable operation to be carried out in a preferred pressure range of from about 50 to about 350 psig. In fact, the stability exhibited by the catalyst of this invention is equivalent to or greater than has heretofore been observed with respect to prior art reforming catalysts at relatively low pressure reforming conditions. Similarly, the temperature required is generally lower than required for a similar reforming operation utilizing prior art reforming catalysts. Preferably, the temperature employed is in the range of from about 900° to about 1,050° F. It is well known in the art that the initial temperature selection is made primarily as a function of the desired octane rating of the product, and the temperature is subsequently adjusted upwardly during the reforming operation to compensate for the inevitable catalyst deactivation that occurs and to provide a constant octane product. It is a feature of the present invention that the required rate of temperature increase to maintain a constant octane product is substantially lower than is required with prior art catalysts including prior art tin-platinum catalysts.

The following example is presented in illustration of this invention and is not intended as an undue limitation on the generally broad scope of the invention as set out in the appended claims.

EXAMPLE I

Gamma-alumina spheres of about 1/16 inch diameter were prepared by the described oil-drop method. Thus, an aluminum chloride hydrosol, prepared by digesting aluminum pellets in dilute hydrochloric acid, was commingled with hexamethylenetetramine and dispersed as droplets in a hot oil bath. The resulting spheres were aged in the oil bath overnight and then washed, dried and calcined. The alumina spheres had an average bulk density of about 0.5 grams/cc and a surface area of about 180 m^2/gm.

In preparing the impregnating solution, an acidic stannous chloride solution was commingled with chlo-

roplatinic acid solution, the resultant solution turning red in color. The stannous chloride solution (17.5 cc) was prepared by dissolving stannous chloride in hydrochloric acid and contained 25 mg. of Sn^{2+}/ml. The chloroplatinic acid solution (65.6 cc) contained 10 mg. of Pt^{4+}/ml. The red colored solution was stabilized with 50 ml of concentrated hydrochloric acid and the solution thereafter diluted to about 300 cubic centimeters with water.

About 350 cubic centimeters of the calcined alumina spheres were immersed in the described impregnating solution in a steam jacketed rotary evaporator, the volume of the impregnating solution being substantially equivalent to the volume of carrier material. The spheres were allowed to soak in the rotating evaporator for about 30 minutes at room temperature and steam was thereafter applied to the evaporator jacket. The solution was evaporated substantially to dryness, and the dried spheres were subsequently calcined in air for about 1 hour at 550° F. and immediately thereafter for about 2 hours at 1000° F. The catalyst particles were then treated in a substantially pure hydrogen stream containing less than about 20 volume ppm H_2O for about 1 hour at 1050° F. to yield the reduced form of the catalyst. The final catalyst product contained 0.375 wt. percent platinum and 0.25 wt. percent tin, calculated as the elemental metal.

The described catalyst composite, hereinafter referred to as Catalyst A, was evaluated for stability under exceptionally severe reforming conditions utilizing a laboratory scale reforming apparatus comprising a reactor column, a high pressure-low temperature product separator, and a debutanizer column. A charge stock, boiling in the 205°-400° F. range and having an octane rating of about 50 F-1 clear, was admixed with hydrogen and charged downflow through the reactor column in contact with 100 cubic centimeters of catalyst disposed in a fixed bed therein. The stability test consisted of six periods, each of which included a 12 hour line-out and a 12 hour test period. The test was designed to measure, on an accelerated basis, the stability characteristics of the catalyst in a high severity reforming operation. Accordingly, hydrogen was admixed with the hydrocarbon charge stock in only a 5:1 mole ratio, and the mixture preheated to about 930° F., and charged to the reactor at a liquid hourly space velocity of 1.5. The reactor inlet temperature was adjusted upward periodically to maintain the C_5+ product octane at 102 F-1 clear. The reactor outlet pressure was controlled at 100 psig. The reactor effluent stream was cooled in the product separator to about 55° F. and a portion of the hydrogen-rich gaseous phase separated and recycled to effect the aforesaid hydrogen/hydrocarbon ratio. The excess separator gas, representing hydrogen make, was measured and discharged. The liquid phase was recovered from the product separator through a pressure reducing valve and treated in the debutanizer column, with a C_5+ product being recovered as debutanizer bottoms.

The results of the stability test are tabulated below with reference to a Catalyst B containing 0.75 wt. percent platinum and with reference to a Catalyst C containing 0.375 wt. percent platinum in combination with 0.22 wt. percent tin. Catalysts B and C were prepared in substantially the same manner as Catalyst A except that conventional impregnating techniques were employed. Thus, Catalyst B was prepared by impregnating the alumina spheres with a chloroplatinic acid solution, and Catalyst C by impregnating the alumina with chloroplatinic acid and stannic chloride solution.

TABLE I

Period No.	Temp. °F.	C_{5+} Vol. %	Debutanizer Gas, SCF/BBL	H_2/HC Mole Ratio
	Catalyst A, 0.375 wt. % Pt., 0.25 wt. % Sn.			
1	968	76.0	78	5:1
2	977	76.1	78	5:1
3	987	75.5	77	5:1
4	992	75.6	78	5:1
5	997	76.6	75	5:1
6	1002	76.5	78	5:1
	Catalyst B, 0.75 wt. % Pt.			
1	978	69.4	108	10:1
2	994	69.9	107	10:1
3	1022	69.8	112	10:1
4	1045	62.5	152	10:1
5	1103	—	—	10:1
6	—	—	—	10:1
	Catalyst C, 0.375 wt. % Pt., 0.22 wt. % Sn.			
1	970	76.4	63	10:1
2	978	77.5	56	10:1
3	986	77.0	56	10:1
4	992	76.3	61	10:1
5	998	76.5	62	10:1
6	999	76.3	62	10:1

While it appears at first glance that Catalyst C is substantially equivalent to Catalyst A with respect to stability, it should be noted that the test provisions were substantially less severe with respect to Catalyst B and C in that the hydrogen/hydrocarbon mole ratio employed was 10:1 as opposed to 5:1 with respect to Catalyst A.

I claim as my invention:

1. A process for reforming a hydrocarbon feed stock which comprises heating said charge stock in contact with a catalytic composite at reforming conditions including a pressure of from about 0 to about 1000 psig and a temperature of from about 800° to about 1100° F., said catalytic composite consisting essentially of a tin component in combination with a platinum component on a carrier material, and prepared by the method which comprises:

a. impregnating a high surface area, porous carrier material with a solution of a complex chlorostannate (II)-chloroplatinate anionic species, said solution being stabilized in contact with said carrier material with an aqueous halogen acid; and

b. drying and calcining the impregnated carrier material.

2. The process of claim **1** further characterized with respect to step (a) in that said solution is stabilized with aqueous hydrochloric acid.

3. The process of claim **1** further characterized with respect to step (a) in that said solution comprises a complex trichlorostannate (II)-chloroplatinate (IV) anionic species.

4. The process of claim **1** further characterized with respect to step (a) in that said solution comprises a complex trichlorostannate (II)-chloroplatinate (II) anionic species.

5. The process of claim **1** further characterized in that said carrier material is an alumina.

6. The process of claim **1** further characterized in that said carrier material is gamma-alumina.

7. The process of claim **1** further characterized with respect to step (a) in that said solution is stabilized with

aqueous hydrochloric acid at a pH of less than about 1.

8. The process of claim **1** further characterized with respect to step (a) in that said carrier material is impregnated with from about 0.05 to about 1.0 wt. percent platinum and from about 0.05 to about 1.0 wt. percent tin from said complex anionic solution.

9. The process of claim **1** further characterized in that said reforming conditions include a pressure of from about 50 to about 350 psig and a temperature of from about 800° to about 1050° F.

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