PATENT SPECIFICATION (11) 1 577 442

1 577 442

(21) Application No. 26258/77 (22) Filed 23 Jun. 1977 (19)

(31) Convention Application No. 699748 (32) Filed 24 Jun. 1976 in

(33) United States of America (US)

(44) Complete Specification Published 22 Oct. 1980

(51) INT. CL.[3] B01J 23/62
C10G 35/09

(52) Index at Acceptance
B1E 1121 1123 1125 1128 1193 1206
1315 1393 1476 1500 1512 1514
1611 1631 1634 1635 1701 1712
1714 1722 1738 1741 1744 DB

(72) Inventor: GEORGE JOHN ANTOS

(54) METHOD OF MANUFACTURING A GERMANIUM/PLATINUM GROUP CATALYST

(71) We, UOP Inc, a corporation organized under the laws of the State of Delaware States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Road, Des Plaines, Illinois, United States of America, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

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 10° - 220°C. range, although it is more often what is commonly called naphtha -- a gasoline fraction characterized by an initial boiling point of from 65° to 120°C. and an end boiling point of from 175° to 220°C.

The reforming of gasoline boiling range feed stocks involves 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, including isomerization, dehydrogenation, dehydrocyclization and hydrocracking of paraffins, and dehydrogenation and ring-isomerization of napthenes, 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-fractional catalyst designed to provide the most favourable 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 the 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 hydro-cracking 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 the 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 an interrelationship between reaction conditions relating to undesirable side reactions and desirable octane-improving reactions. Reaction conditions selected to optimize a particular octane-improving reaction may also promote one or more undesirable side reactions. For example, some hydrocracking is desirable since it produces lower boiling hydrocarbons of

higher octane value than the feed hydrocarbons, but hydrocracking of the lower boiling C_6-C_8 constituents is not desirable since this produces still lower boiling hydrocarbons, such as butane, which are of marginal utility. This is excessive hydrocracking and is to be avoided. The extend 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 (dehydrogenation of paraffins and naphthenes) are net producers of hydrogen and are 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, for their general activity with respect to each other 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 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 bimetallic catalysts to make low-pressure reforming and all the advantages attendant therewith a reality. In particular, a germanium-promoted platinum catalyst has achieved commercial acceptance on a wide scale as a reforming catalyst.

It is generally recognized that catalysis involves a mechanism particularly noted for its unpredictability. Minor variations in the 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 improved activity, selectively and/or stability realized with respect to one or more hydrocarbon conversion reactions. For example, it has been discovered that the aforementioned germanium-promoted platinum catalyst, modified in the course of manufacture with respect to the method of impregnating said platinum and germanium components on the carrier material, exhibits improved activity stability over prior art germanium-promoted platinum reforming catalyst.

This invention seeks to produce an improved reforming catalyst containing a platinum component and a germanium component, particularly suitable for low-pressure reforming and characterized by a novel method of preparation.

According to the present invention there is provided a method of catalyst manufacture which comprises preparing a common non-aqueous solution of a soluble platinum group metal compound and a halo-substituted germane containing less than four halo substituents, impregnating a porous carrier material with said solution, and drying and calcining the impregnated carrier material.

Initially, in accordance with the method of this invention, a halo-substituted germane and a platinum group metal compound are prepared in a common non-aqueous solution to deposit a germanium component and a platinum group metal component on a porous carrier material. The platinum group metal component is preferably platinum, although rhodium, ruthenium, osmium, iridium, and particularly palladium, are also suitable components. The non-aqueous solution is suitably an absolute alcohol solution, absolute ethanol being preferred. Platinum group metal compounds for use in said non-aqueous solution include chloroplatinic acid, platinum chloride, ammonium chloroplatinate, dinitrodiaminoplatinum, palladium chloride, chloropalladic acid, rhodium chloride, ruthenium chloride, ruthenium oxide, osmium chloride and iridium chloride. Chloroplatinic acid is a preferred platinum group metal compound for use herein. In general the selected platinum group metal compound is utilized in an amount to provide a catalyst product containing from 0.05 to 1 wt.% platinum group metal.

The halo-substituted germanes for use in the invention contain less than four halo substituents. Preferably, the halo-substituted germane present in common solution with the platinum group metal compound is a chlorogermane, in particular chlorogermane, dichlorogermane or trichlorogermane. Other suitable halo-substituted germanes are the corresponding fluoro-, bromo-, and iodo-substituted germanes, in particular the normally liquid bromogermane, dibromogermane and tribromogermane. The selected halo-substituted germane is preferably employed in an amount to provide a catalyst product containing from 0.05 to 1 wt.% germanium. The most preferred halo-substituted germane is trichlorogermane.

The improvement in catalytic activity stability observed in the practice of this invention is believed to result from the formation of a complex of the halo-substituted germane with the

platinum group metal compound whereby the germanium and platinum group metal components are deposited and distributed on the surface of the carrier metal in intimate association to realize more fully the synergistic potential of said components heretofore observed with respect to the catalytic conversion of hydrocarbons, particularly catalytic reforming.

Suitable carrier materials include any of the solid adsorbent materials generally utilized as a catalyst support or carrier material, such as the various charcoals, preferably heat treated or chemically treated and generally defined as activated carbon; also the naturally occurring clays silicas and silicates for example, diatomaceous earth (kieselguhr), fuller's earth, attapulgus clay, feldspar, montmorillonite, halloysite and kaolin, the naturally occurring or synthetically prepared refractory inorganic oxides, such as alumina, silica, zirconia, thoria and boria, or combinations, such as silica-alumina, silica-zirconia and alumina-zirconia. Preferably, the surface area is at least 25 square meters per gram. The preferred carrier materials for the present invention are the refractory inorganic oxides, with best results being obtained with an alumina, preferably a porous, adsorptive, high surface area alumina characterized by a surface area of from 25 to 500 square meters per gram. Suitable aluminas thus include gamma-alumina, eta-alumina, and theta-alumina, with gamma-alumina being preferred. Particularly preferred is gamma-alumina characterized by an apparent bulk density of from 0.30 to 0.90 grams per cubic centimeter, an average pore diameter of from 50 to 150 Angstroms, an average pore volume of from 0.10 to 1.0 cubic centimeters per gram, and a surface area of from 150 to 500 square meters per gram.

The alumina employed may be a naturally occurring alumina or it may be synthetically prepared, and may be employed in a shape or form determinative of the shape or form of the final catalyst composition, e.g., spheres, pills, granules, extrudates or powder.

Impregnating conditions employed herein can be those conventional in the art, whereby the catalytic component, or soluble compounds thereof, are adsorbed on the carrier metal 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 relatively brief period, preferably for at least 30 minutes, and the impregnating solution thereafter evaporated substantially to dryness at an elevated temperature.

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 may be 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.

Regardless of the details of how the components of the catalyst are combined with the porous carrier material, the final catalyst composite will be dried and calcined, generally in an oxidizing atmosphere such as air at a temperature of from 200° to 760°C. The catalyst particles are advantageously calcined in stages to minimize breakage. Thus, the catalyst particles are advantageously calcined for a period of from 1 to 3 hours in an air atmosphere at a temperature of from 200° to 375°C., and immediately thereafter at a temperature of from 475° to 650°C. in an air atmosphere for a period of from 3 to 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 20:1 to 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 0.6 to 1.2 wt.%.

It is preferred that the resultant calcined catalytic composite be subjected before use, to a substantially water-free reduction step to ensure 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 suitably contacted with the oxidized catalyst at a temperature of from 427° to 649°C., and the reduction 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 is suitably

effected at a pressure of from 1 to 68 atmospheres, abs. and at a temperature of from 425° to 595°C. and preferably in the range of from 475° to 565°C. The catalyst permits a stable operation to be carried out in a preferred pressure range of from 3.4 to 24 atms., gauge. In fact, the stability exhibited by the catalyst manufactured according to this invention is equivalent to or greater than has heretofore been observed with respect to prior art reforming catalyst at relatively low-pressure reforming conditions. Similarly, the temperature initially required to produce a desired octane rating of the product, as well as the rate of temperature increase required to maintain a constant octane product are both substantially lower than required for a similar reforming operation with prior art catalysts, including prior art germanium-platinum catalysts.

Although the catalyst composition manufactured according to this invention is most suitable for reforming, it may be used to promote other reactions including dehydrogenation of specific hydrocarbons or hydrocarbon fractions, isomerization of specific hydrocarbons or hydrocarbon fractions, destructive hydrogenation or hydrocracking of larger hydrocarbon molecules such ass those occurring in the kerosine and gas oil boiling range, and the oxidation of hydrocarbons to produce first, second and third stage oxidation products. Reaction conditions employed in the various hydrocarbon conversion reactions may be those heretofore practised in the art. For example, alkylaromatic isomerization reaction conditions which may be used include a temperature of from 0° to 535°C., a pressure of from atmospheric to 103 atms. abs., a hydrogen-to-hydrocarbon mole ratio of from 0.5:1 to 20:1 and a LHSV of from 0.5 to 20. Likewise, typical hydrocracking reaction conditions which may be used include a pressure of from 35 to 205 atsm. abs., a temperature of from 200° to 500°C., a LHSV of from 0.1 to 10, and a hydrogen circulation rate of from 178 to 1780 cubic meters per cubic meter of charge.

The following examples are presented in illustration of the method of this invention.

Example I

Gamma-alumina spheres of about 1.6 mm. diameter were prepared by the well-known 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/g.

In preparing the impregnating solution, trichlorogermane and chloroplatinic acid were dissolved in absolute ethanol to form a common solution thereof. The solution was stabilized with a quantity of HCl equivalent to about 3 wt.% of the alumina to be impregnated. The solution was thereafter diluted to about 300 cubic centimeters.

About 350 centimeters of the calcined alumina spheres were immersed in the 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 dried in air for about 1 hour at 150°C. and immediately thereafter calcined in air for about 2 hours at 525°C. The catalyst particles were then treated in a substantially pure hydrogen stream containing less than 20 volume ppm. H_2O for about 1 hour at 565°C. to yield the reduced form of the catalyst. The final catalyst product contained 0.375 wt. % platinum and 0.25 wt. % germanium calculated as the elemental metal.

The described catalyst composite, hereinafter referred to as Catalyst A, was evaluated for activity stability 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 95° - 205°C. 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-rich recycle gas was admixed with the hydrocarbon charge stock in a 10:1 mole ratio, and the mixture preheated to about 500°C. and charged to the reactor at a liquid hourly space velocity of 3.0. The reactor inlet temperature was adjusted upward periodically to maintain the C_5+ product octane at 100 F-1 clear. The reactor outlet pressure was controlled at 21.4 atms. abs. The reactor effluent stream was cooled in the product separator to about 13°C. and a portion of the hydrogen-rich gaseous phase separated and recycled to effect the aforesaid recycle gas/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 C_5+ product being recovered as debutanizer bottoms.

The results of the stability test are tabulated below with reference to Catalyst B containing 0.375 wt. % platinum in combination with 0.25 wt. % germanium. Catalyst B was 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 an aqueous solution of chloroplatinic acid and germanium tetrachloride.

TABLE I

Period No.	Temp. °C.	C_5+ Yield, Vol. %
Catalyst A		
1	540	72.21
2	542	71.73
3	543	--
4	545	71.11
5	546	--
6	547	71.16
Catalyst B		
1	540	--
2	543	70.79
3	545	--
4	547	70.70
5	549	--
6	552	70.48

It is apparent that the rate of temperature increase required to maintain the C_5+ product octane at 100 F-1 clear is appreciably less with respect to the catalyst prepared by the method of the invention.

WHAT WE CLAIM IS:-

1. A method of catalyst manufacture which comprises
(a) preparing a common non-aqueous solution of a soluble platinum group metal compound and a halo-substituted germane containing less than four halo substituents;
(b) impregnating a porous carrier material with said solution; and
(c) drying and calcining the impregnated carrier material.

2. The method of Claim 1 further characterized in that said soluble platinum group metal compound is a platinum compound.

3. The method of Claim 2 further characterized in that said platinum compound is chloroplatinic acid.

4. The method of any of Claims 1 to 3 further characterized in that said halo-substituted germane is a chloro-substituted germane.

5. The method of Claim 4 further characterized in that said chloro-substituted germane is trichlorogermane.

6. The method of any of Claims 1 to 5 further characterized in that said non-aqueous solution is an alcoholic solution.

7. The method of Claim 6 further characterized in that the solvent is absolute ethanol.

8. The method of any of claims 1 to 7 further characterized in that said carrier material is a refractory inorganic oxide.

9. The method of claim 8 further characterized in that said carrier material is an alumina carrier material.

10. The method of any of claims 1 to 9 further characterized in that said carrier material has a surface area of at least 25 square meters per gram.

11. The method of any of Claims 1 to 10 further characterized in that said germane is utilized in an amount to provide a catalyst product containing from 0.05 to 1 wt. % germanium.

12. The method of any of Claims 1 to 11 further characterized in that said platinum group metal compound is utilized in an amount to provide a catalyst product containing from 0.05 to 1 wt. % platinum group metal.

13. The method of any of Claims 1 to 12 further characterized in that said impregnated

carrier material is dried and calcined at a temperature of 200° to 760°C.

14. The method of Claim 13 further characterized in that the impregnated carrier material is dried, then calcined for a period of 1 to 3 hours at a temperature of 200° to 375°C. and then further calcined for a period of 3 to 5 hours at a temperature of 475° to 650°C.

15. The method of any of Claims 1 to 14 further characterized in that the calcined composite is reduced by subjecting the same to contact with substantially pure and dry hydrogen at a temperature of from 427° to 649°C.

16. Catalyst whenever prepared by the method of any of the foregoing Claims 1 to 15.

17. A process for the reforming of a gasoline boiling range feed stock which comprises subjecting said feed stock to contact, at reforming conditions and in the presence of hydrogen, with a catalyst prepared in accordance with the method of any of the foregoing Claims 1 to 15.

J.Y. & G.W. JOHNSON,
Furnival House,
14-18 High Holborn,
London, WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,from
which copies may be obtained.