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Bertolacini et al.

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[54] **REFORMING PETROLEUM HYDROCARBONS WITH GALLIUM-PROMOTED CATALYSTS**

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[52] **U.S. Cl.** **208/65**
[51] **Int. Cl.** **C10g 39/00**
[58] **Field of Search** .... 208/65; 252/442, 252/466 PT

[56] **References Cited**

UNITED STATES PATENTS

2,814,599	11/1957	Lefrancois et al.	252/466
2,914,464	11/1959	Burton et al.	208/138
2,999,074	9/1961	Bloch et al.	252/442

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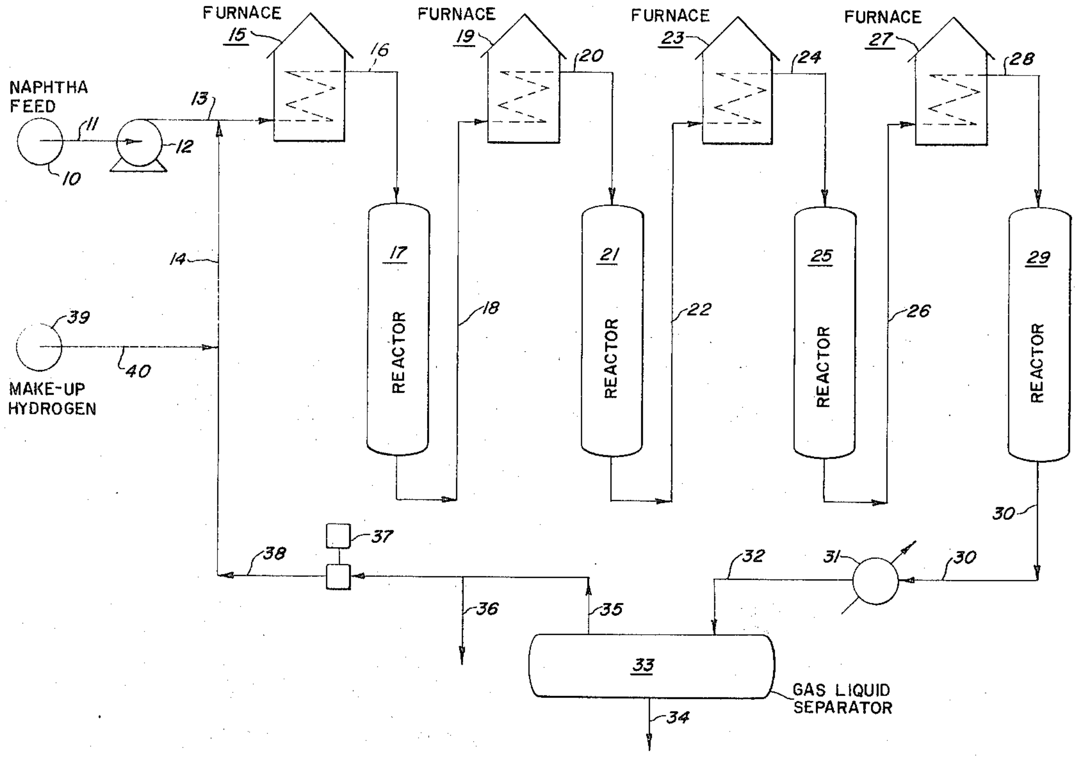
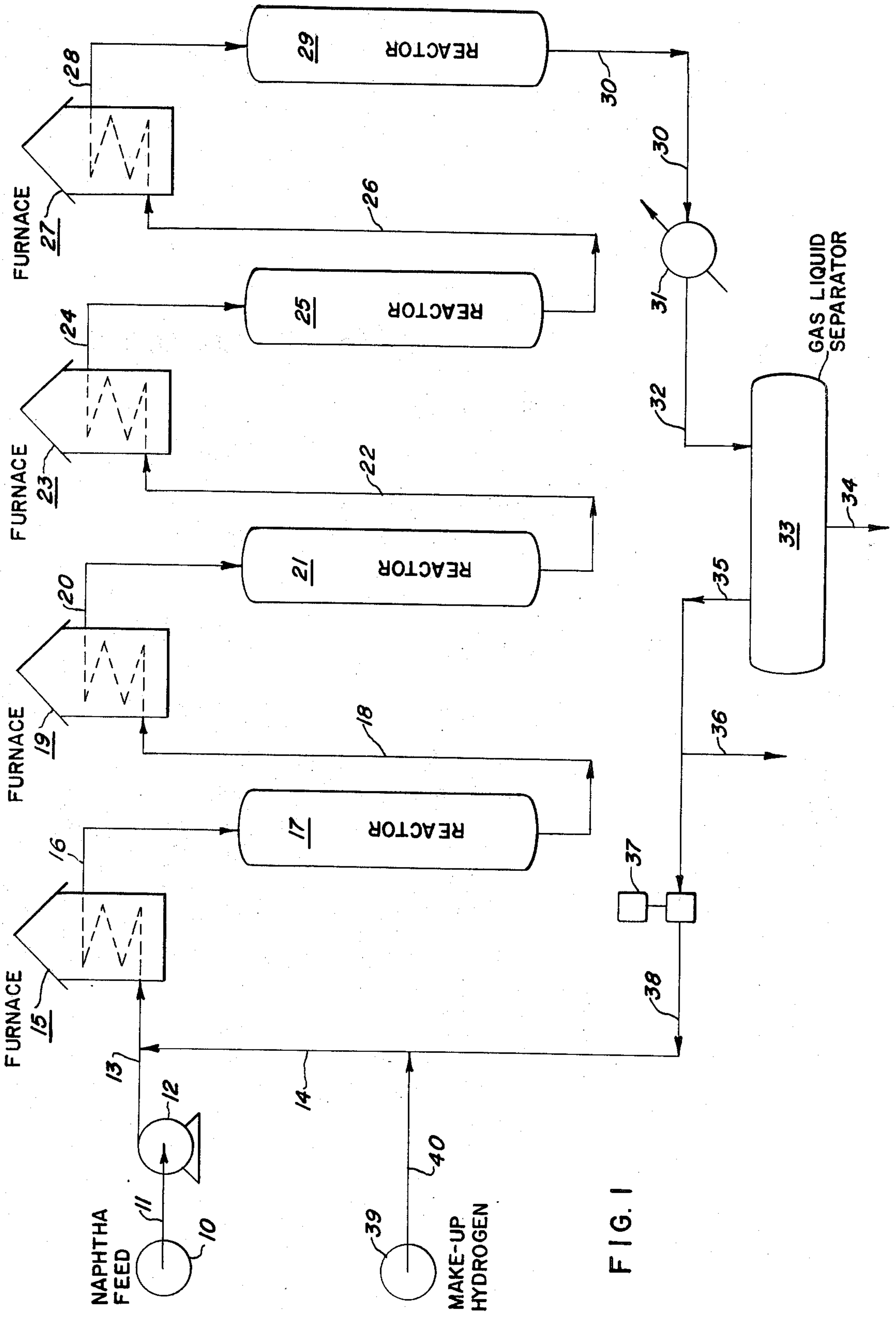
[57] **ABSTRACT**

There is provided a process for reforming a petroleum hydrocarbon stream, which process comprises contacting said hydrocarbon stream in a first reforming zone under reforming conditions and in the presence of hydrogen with a first reforming catalyst to produce a first reformate and subsequently contacting said first reformate in a second reforming zone under reforming conditions and in the presence of hydrogen with a second catalyst comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide. The first reforming catalyst may be any suitable reforming catalyst in the art.

38 Claims, 2 Drawing Figures




NAPHTHA FEED
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REACTOR 25
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FURNACE 27
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REACTOR 29
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GAS LIQUID SEPARATOR
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MAKE-UP HYDROGEN
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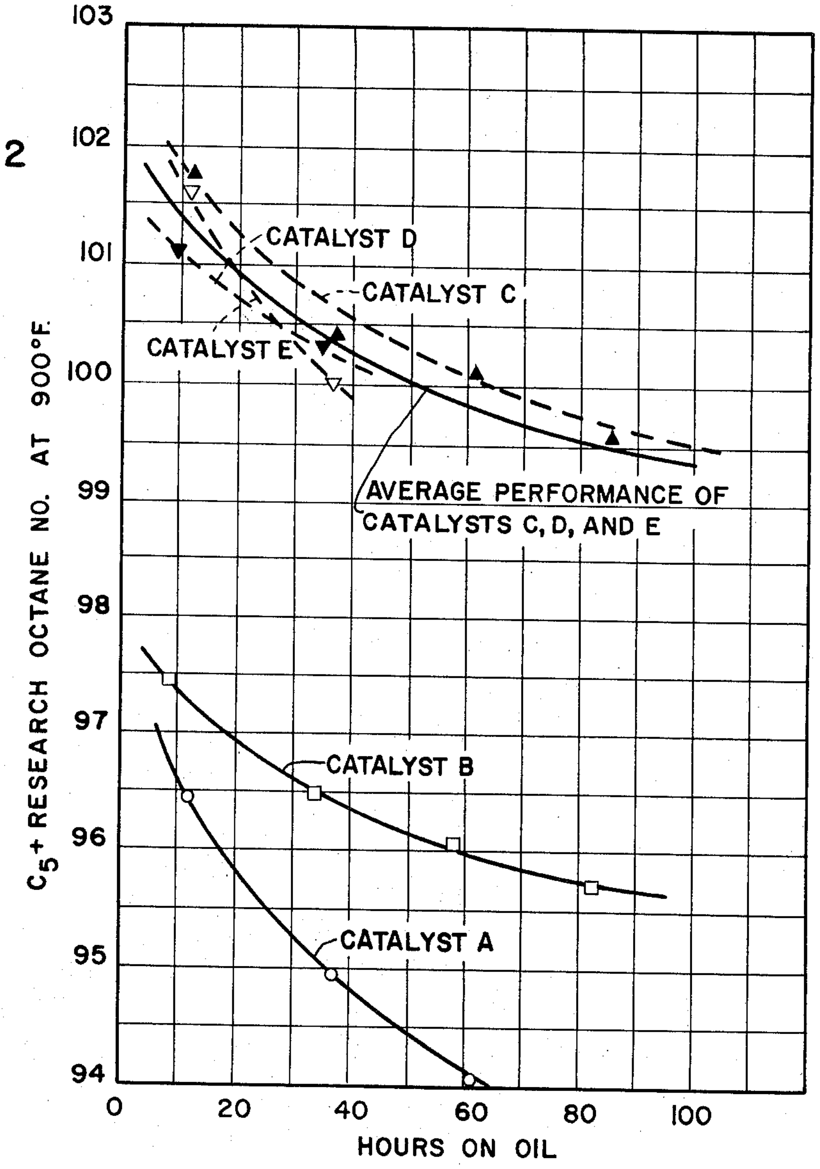
FIG. 1

FIG. 2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C_5+ RESEARCH OCTANE NO. AT 900°F.
HOURS ON OIL
CATALYST D
CATALYST C
CATALYST E
AVERAGE PERFORMANCE OF CATALYSTS C, D, AND E
CATALYST B
CATALYST A

REFORMING PETROLEUM HYDROCARBONS WITH GALLIUM-PROMOTED CATALYSTS

BACKGROUND OF THE INVENTION

The reforming of petroleum hydrocarbon streams is one of the important petroleum refining processes that may be employed to provide high-octane-number hydrocarbon blending components for gasoline. In the typical reforming process, the reactions comprise dehydrogenation reactions, isomerization reactions, and hydrocracking reactions. The dehydrogenation reactions include the dehydrogenation of cyclohexanes to aromatics, the dehydroisomerization of alkylcyclopentanes to aromatics, the dehydrogenation of paraffins to olefins, and the dehydrocyclization of paraffins and olefins to aromatics. The isomerization reactions include isomerization of n-paraffins to isoparaffins, the hydroisomerization of olefins to isoparaffins, the isomerization of alkylcyclopentanes to cyclohexanes, and the isomerization of substituted aromatics. The hydrocracking reactions include hydrocracking of paraffins and hydrodesulfurization. Adequate discussion of the reactions occurring in a reforming reaction zone are presented in CATALYSIS, Vol. VI, P. H. Emmett, editor, Reinhold Publishing Corporation, 1958, pages 497–498, and PETROLEUM PROCESSING, R. J. Hengstebeck, McGraw-Hill Book Company, Inc., 1959, pages 179–184.

It is well known by those skilled in the art that several catalysts are capable of reforming petroleum naphthas and hydrocarbons that boil in the gasoline boiling range. Although reforming may be carried out through the use of molybdena-on-alumina catalysts, chromium-oxides-on-alumina catalysts, platinum-halogen-on-alumina catalysts, and platinum-aluminosilicate-material-alumina catalysts, the catalysts employing platinum as a hydrogenation component are generally employed today in the reforming processes of the petroleum industry.

Moreover, it is known by those skilled in the art that a platinum-containing reforming catalyst may be promoted by a small amount of gallium. This is taught in U.S. Pat. No. 2,814,599.

It has now been found that a catalytic composition comprising a hydrogenation component and a small amount of gallium supported on a refractory inorganic oxide may be suitably employed in the last reactor, or possibly the last two reactors in a multiple-reactor reforming system. Such a reforming system will provide high-octane number blending material for unleaded and/or low-lead motor fuels.

SUMMARY OF THE INVENTION

Broadly, according to the present invention, there is provided a process for the reforming of a petroleum hydrocarbon stream, which process comprises contacting said hydrocarbon stream in a first reforming zone under reforming conditions and in the presence of hydrogen with a first reforming catalyst to produce a first reformate and subsequently contacting said first reformate in a second reforming zone under reforming conditions and in the presence of hydrogen with a second catalyst comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide. The second catalyst may contain a halide, preferably, chloride.

The preferred hydrogenation component of the second catalyst is a Group VIII noble metal, particularly platinum. The preferred refractory inorganic oxide is a catalytically active alumina. Gallium may be present in an amount of about 0.05 wt. % to about 3 wt. %, calculated as the element and based upon the total weight of the second catatlyic composition. Preferably, gallium is present in an amount of about 0.1 wt. % to about 1 wt.%.

In another embodiment of the process of the present invention, a mildly-reformed or partially-reformed naphtha is reformed further over a catalyst comprising a hydrogenation component and a small amount of gallium supported on a porous refractory inorganic oxide. This embodiment comprises contacting a mildly-reformed or partially-reformed naphtha in a reforming zone under reforming conditions and in the presence of hydrogen with a catalytic composition comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Two Figures accompany this document.

FIG. 1 presents a simplified schematic flow diagram of a preferred embodiment of the process of the present invention, wherein the gallium-containing catalytic composition is employed in the last reactor, or tail reactor, of a multiple-reactor reforming system.

FIG. 2 provides a comparison of several catalysts, when each is employed in a test simulating a tail-reactor operation.

DESCRIPTION AND PREFERRED EMBODIMENTS

The highly mechanized society of today requires an increasing demand for very-high-octane-number motor fuels. The process of this invention is especially advantageous for the production of high-octane-number blending components for motor fuels by means of the reforming of petroleum naphthas and petroleum hydrocarbon streams boiling in the gasoline boiling range. It may be employed suitably to produce high-octane-number blending components for unleaded and/or low-lead motor fuels.

The process of the present invention may be used to reform a feedstock which is a member selected from the group consisting of a virgin naphtha, a cracked naphtha, a hydrocarbon fraction boiling in the gasoline boiling range, and mixtures thereof. It may also be used to reform partially-reformed naphthas and other hydrocarbon streams. A naphtha will exhibit a boiling range of about 70°F. to about 500°F., preferably, about 180°F. to about 400°F. The gasoline boiling range comprises temperatures of about 120°F. to about 420°F., preferably, about 140°F. to about 380°F. The partially-reformed hydrocarbon streams will exhibit an unleaded research octane number within the range of about 75 to about 95. As used herein, the terms "mildly-reformed" and "partially-reformed" refer to such streams as have been reformed to an unleaded research octane number of about 75 to about 95.

Since many of the above feedstocks may contain appreciable amounts of nitrogen and sulfur compounds, which are deleterious to the first catalyst of that embodiment of the present invention which employs a multiple-catalyst reforming system, it is preferred that the feedstock in this case be subjected to a suitable hydrodesulfurization and/or hydrodenitrogenation treatment, such as hydrofining, prior to use in the embodiment of the process of the present invention in order to reduce both the nitrogen and sulfur levels to tolerable limits.

According to the process of the present invention, there is provided a process for reforming a petroleum hydrocarbon stream, which process comprises contacting said hydrocarbon stream in a first reforming zone under reforming conditions and in the presence of hydrogen with a first reforming catalyst to produce a first reformate and subsequently contacting said first reformate in a second reforming zone under reforming conditions and in the presence of hydrogen with a second reforming catalyst comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide. In another embodiment, the process comprises contacting a partially-reformed hydrocarbon stream in a reforming zone under reforming conditions and in the presence of hydrogen with a catalytic composition comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide.

The first reforming catalyst, i.e., the catalyst that is employed in the first reforming zone of the multiple-reforming-zone embodiment of the process of the present invention, may be typically a reforming catalyst comprising a platinum group metal and a halide supported on a catalytically active alumina. It is contemplated that such catalyst may be promoted with a small amount of rhenium. It is to be understood that any suitable reforming catalyst in the art may be employed as the first catalyst in the first reforming zone. A particular first catalyst is a catalyst consisting essentially of a platinum group metal, rhenium, and a halide on a catalytically active alumina. A preferred first catalyst is a catalyst which comprises about 0.1 wt.% to about 2 wt.% platinum, about 0.05 wt.% to about 2 wt.% chloride, and about 0.05 wt.% to about 2 wt.% rhenium on a catalytically active alumina and which does not contain gallium. The catalytically active alumina that is employed as the support material for the first catalyst may be any catalytically active alumina, such as gamma-alumina or eta-alumina. Such alumina should have an average pore diameter of about 70 A to about 200 A, or larger. The alumina should have a surface area of at least 150 square meters per gram. Suitably, the surface area should be within the range of about 200 to about 800 square meters per gram, or larger.

The second reforming catalyst, i.e., the catalyst that is employed in the second reforming zone of the process of the present invention, is a catalytic composition which comprises a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide.

Suitable hydrogenation components that are employed in a typical reforming catalyst, and that may be employed in the second reforming catalyst of the process of the present invention, include Group VI metals of the Periodic Table of Elements, particularly, molybdenum and chromium, the oxides of Group VI metals, and Group VIII metals, particularly, the Group VIII noble metals. The Group VIII noble metals include ruthenium, rhodium, palladium, osmium, iridium, and platinum. The preferred Group VIII noble metal is platinum.

When the hydrogenation component of the second reforming catalyst comprises a Group VIII noble metal, the hydrogenation component may be present in an amount of about 0.05 wt.% to about 2 wt.%, calculated as the element and based upon the total weight of the catalyst. Preferably, the Group VIII noble metal is present in an amount of about 0.1 wt.% to about 1 wt.%, calculated as the element and based upon the total weight of the catalyst.

Another essential component of the second reforming catalyst is gallium, a member of Group III of the Periodic Table of Elements. Gallium may be present in an amount of about 0.05 wt.% to about 3 wt.%, calculated as the element and based upon the total weight of the catalytic composition. Preferably, gallium is present in an amount of about 0.1 wt.% to about 1 wt.%.

The solid catalytic support of the second reforming catalyst of the process of the present invention comprises a porous refractory inorganic oxide. The preferred refractory inorganic oxide is a catalytically active alumina, such as gamma-alumina, eta-alumina, or mixtures thereof. The properties of such alumina are presented hereinabove. The solid catalytic support may also contain a crystalline aluminosilicate material. Such aluminosilicate material is a large-pore aluminosilicate material and preferably possesses pores within the range of about 5 A to about 20 A. A preferred aluminosilicate material is mordenite or faujasite. Suitably, the aluminosilicate material is suspended in and distributed throughout a matrix of the porous refractory inorganic oxide. The aluminosilicate material may be present in an amount of about 0.5 wt.% to about 25 wt.%, based upon the weight of the catalytic support. Preferably, the large-pore crystalline aluminosilicate material has been cation-exchanged with a member selected from the group consisting of an alkaline earth metal, a rare earth metal, hydrogen, and a hydrogen precursor, such as ammonium, to reduce the alkali-metal content of the alumino-silicate material to a level that is less than 1 wt.%, calculated as the metal.

The second reforming catalyst of the process of the present invention may also contain a halide. Suitable halides are chlorides and fluorides. The preferred halide is a chloride. The halide may be present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of the second reforming catalyst. Preferably, the halide is present in an amount of about 0.1 wt.% to about 1 wt.%, based upon the weight of the second reforming catalyst.

The second reforming catalyst of the process of the present invention may be prepared in various ways. For example, a soluble compound of the hydrogenation metal and a soluble compound of the gallium may be added to a sol or gel of the refractory inorganic oxide. This composition may be thoroughly blended and the sol or gel mixture may be subsequently co-gelled by the addition of dilute ammonia. The resulting cogelled material may then be dried and calcined. If an aluminosilicate material is to be a component of the catalytic composition, it may be added in a finely divided form to the sol or gel of the refractory inorganic oxide and suitable compounds of the hydrogenation component and gallium may be added thereto, and the resulting composition may then be thoroughly blended prior to co-gelling, drying, and calcining. In another method of preparation, the refractory inorganic oxide is gelled, dried, pelleted, calcined, and cooled, and the resulting composition is then impregnated with a solution of the hydrogenation component and/or a solution of gallium. Suitable calcination conditions comprise a temperature in the range of about 900°F. to about 1,100°F. and a calcination time of about 1 to about 20 hours. Suitable drying conditions comprise a temperature in the range of about 200°F. to about 400°F. and a drying time of about 3 to about 30 hours. Preferably, drying conditions comprise a temperature of about 250°F. for about 8 to about 16 hours and calcination conditions comprise a temperature of about 1,000°F. for about 2 to about 6 hours. The halide may be incorporated into the catalytic composition as a halide of the hydrogenation metal, or as a halogen acid or a halide salt.

It is contemplated that the second reforming catalyst could contain some rhenium and that such could be incorporated into the catalytic composition in a suitable manner, e.g., by impregnation.

The second reforming catalyst of the process of the present invention is suitable for the conversion of petroleum hydrocarbon streams. In particular, it is employed for the reforming of petroleum hydrocarbon naphthas and those petroleum hydrocarbon streams boiling in the gasoline boiling range. This second reforming catalyst is effective for converting the heavy paraffins remaining in a reformate. Therefore, a preferred embodiment of the process of the present invention is a process which employs a first reforming catalyst comprising a platinum group metal and a halide on a catalytically active alumina in a first reforming zone and a second reforming catalyst comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a catalytically active alumina in a second reforming zone. Still more particularly, the first reforming catalyst is employed in all of the reactors except the tail reactor and the second reforming catalyst is employed in the tail reactor. For selected conditions and selected feedstocks, it is contemplated that the first reforming zone could constitute two or more reactors and the second reforming zone could constitute at least one reactor. In an alternative embodiment of the process of the present invention, the reforming system could comprise one or more reactors containing a catalyst that is the same as the second reforming catalyst in the two-catalyst embodiment of the process of the present invention and making up a sole reaction zone. To this latter embodiment, a partially-reformed naphtha would be the suitable feedstock.

According to one embodiment of the process of the present invention, there is provided a process for reforming a petroleum hydrocarbon stream, which process comprises contacting a partially-reformed hydrocarbon stream in a reforming zone under reforming conditions and in the presence of hydrogen with a catalyst comprising a hydrogenation component and a small amount of gallim on a solid catalytic support comprising a porous refractory inorganic oxide. In another embodiment of the process of the present invention, the process comprises contacting a petroleum hydrocarbon stream in a first reforming zone under reforming conditions and in the presence of hydrogen with a first reforming catalyst to produce a first reformate and subsequently contacting said first reformate in a second reforming zone under reforming conditions and in the presence of hydrogen with a second reforming catalyst comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide. This latter embodiment is a process wherein the first reforming zone comprises two or more reactors and the second reforming zone comprises at least one reactor.

Typical operating conditions of this reforming process comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a weight hourly space velocity (WHSV) of about 0.5 to about 10 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 standard cubic feet per barrel (SCFG) to about 15,000 SCFB. Preferred reforming conditions comprise an average catalyst temperature of about 850°F. to about 950°F., a pressure of about 50 psig to about 300 psig, a WHSV of about 1 to about 8 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 3,000 SCFB to about 10,000 SCFB. These operating conditions are appropriate for each reforming zone of the multiple-zone embodiment of the process of the present invention.

The process of the present invention can be carried out in any of the conventional types of equipment known to the art. One may, for example, employ catalysts in the form of pills, pellets, granules, broken fragments, or various special shapes, disposed as one or more fixed beds within one or more reaction zones, and the charging stock may be passed therethrough in the liquid, vapor, or mixed phase, and in either upward or downward flow. Alternatively, the catalysts may be in a suitable form for use in moving beds, in which the charging stock and catalyst are preferably passed in countercurrent flow; or in fluidized-solid processes, in which the charging stock is passed upward through a turbulent bed of finely divided catalyst; or in the suspensoid process, in which the catalyst is slurried in the charging stock and the resulting mixture is conveyed into the reaction zone. A fixed-bed reforming process is exemplified by Ultraforming (Petroleum Engineer, Vol. XXVI, No. 4, April 1954, at page C-35). In a six-reactor unit with the five fixed-bed reactors on oil and one fixed-bed reactor under regeneration, it is convenient to employ the second reforming catalyst in the last reactor and a mixture (or layers) of the first reforming catalyst and the second reforming catalyst in the swing reactor. The reaction products from any of the foregoing processes are removed from the reaction zones and fractionated to recover the various components thereof. The hydrogen and unconverted materials are recycled as desired, the excess hydrogen produced in the reformer conveniently being utilized in the hydrodesulfurization of the feed.

Unwanted products in the reforming of petroleum hydrocarbon streams are light hydrocarbon gases and coke. Such products and other compounds, such as polynuclear aromatics and heavy hydrocarbons, may result in coke. As the operation progresses, a substantial amount of coke accumulates on the surface of each of the catalysts resulting in an increasingly rapid rate of catalyst deactivation. Consequently, the coke must be removed periodically from the surface. Such coke removal may be accomplished through a coke-burn treatment wherein the coked catalyst is contacted with an oxygen-containing gas at selected temperatures. Typically, the gas will contain oxygen within the range of about 1.0 volume percent to about 21 volume percent. The concentration of oxygen in the gas should be maintained at a level which will not result in the production of temperatures that will be in excess of 1,100°F., preferably, in excess of 1,050°F.

The process of the present invention may be employed typically as a semi-regenerative reforming process or as a regenerative or cyclic process.

In a semi-regnerative reforming process, the flow of hydrocarbons is stopped to all of the reactors and the catalyst in each of the reactors is regenerated. In a regenerative or cyclic reforming system, one of the reactors is removed from the system and is replaced by an auxiliary reactor. Reforming of petroleum hydrocarbons continues in such a system while catalyst in the reactor that has been removed from the system is regenerated. The auxiliary reactor is known as a swing reactor. It is contemplated in the process of the present invention that the multiple-reactor system may include either one swing reactor or two swing reactors. When two swing reactors are being employed, one will contain the catalyst that is employed in the first reforming zone of the process and will be used to replace a reactor in the first reforming zone. The other will contain the catalyst that is employed in the second reforming zone and will be used to replace a reactor in the second reforming zone.

Either the first reforming catalyst or the second reforming catalyst that is employed in the process of the present invention is capable of being regenerated and is capable of withstanding the conditions employed in the regeneration treatment.

A preferred embodiment of the process of the present invention is depicted in the accompanying FIG. **1.** This figure is a simplified schematic flow diagram of the preferred embodiment. It does not include certain auxiliary equipment, such as heat exchangers, valves, pumps, compressors, and associated equipment, which would be needed in various places along the flow path of the process in addition to the pump and compressor that are depicted in the drawing. Such additional auxiliary equipment and its location requirements would be quickly recognized by one having ordinary skill in the art. Therefore, such equipment is not shown in the figure.

In the embodiment represented in FIG. **1**, a naphtha heart cut, having a boiling range of about 160°F. to about 400°F., preferably, about 180°F. to about 380°F., is obtained from source **10.** This feedstock is passed through line **11** into pump **12**, which pumps the hydrocarbons through line **13.** Hydrogen-containing recycle gas is introduced into line **13** via line **14** to be mixed with the hydrocarbons in line **13.** The resulting hydrogen-hydrocarbon mixture passes through line **13**, furnace **15**, and line **16** into the top of reactor **17.** The material is introduced into reactor **17** at a temperature of about 940°F. to about 980°F. The outlet temperature of reactor **17** is approximately 800°F. and the pressure in reactor **17** is within the range of about 160 psig to about 320 psig.

The effluent from reactor **17** passes through line **18**, furnace **19**, and line **20** into the top of reactor **21.** Sufficient heat is introduced into this hydrogen-hydrocarbon stream by furnace **19** so that the temperature at the inlet of reactor **21** is about 960°F. to about 1,000°F. The outlet temperature of reactor **21** is approximately 855°F. and the pressure in reactor **21** is within the range of about 140 psig to about 300 psig.

The effluent from reactor **21** passes through line **22**, furnace **23**, and line **24** into the top of reactor **25.** This effluent is heated in furnace **23** so that the inlet temperature of reactor **25** is about 960°F. to about 1,000°F. The outlet temperature of reactor **25** is approximately 940°F. and the pressure in reactor **25** is within the range of about 120 psig to about 280 psig.

The effluent from reactor **25** passes through line **26**, furnace **27**, and line **28** into the top of reactor **29.** This hydrocarbon effluent is heated in furnace **27** so that the inlet temperature of reactor **29** is about 980°F. to about 1,020°F. The outlet temperature of reactor **29** is about 950°F. and the pressure in reactor **29** is within the range of about 100 psig to about 260 psig.

Reactors **17**, **21**, and **25** all contain a catalyst comprising platinum and chloride on a support of catalytically active alumina. The catalyst may be promoted by a small amount of rhenium. In general, the catalyst contains 0.1 to about 2 wt.% platinum and 0.1 to 5 wt.% chloride, preferably, 0.4 to 1 wt.% chloride. The fourth reactor, or tail reactor, in the system contains a second reforming catalyst comprising about 0.1 wt.% to about 1 wt.% platinum, about 0.1 wt.% to about 1 wt.% gallium, and about 0.1 wt.% to about 1 wt.% chloride on a gamma-alumina, each amount being based upon the weight of the second reforming catalyst.

Not shown in the figure is a fifth reactor, which reactor contains a mixture or layers of the two catalysts. This additional reactor is employed as a swing reactor for each of the four reactors in this system when the catalyst in a particular reactor has become deactivated and must be regenerated. The reactor containing this deactivated catalyst is removed from the system and is replaced by the swing reactor in order that the reforming system may be operated continuously, even though the deactivated catalyst has been removed from the system and is being regenerated.

The hydrogen-to-hydrocarbon ratio and the WHSV employed in the various reactors fall within the respective ranges of values as expressed hereinabove.

The effluent from reactor **29** passes through line **30**, water cooler **31**, and line **32** into gas-liquid separator **33.** Gas-liquid separator **33** is operated at a pressure of about 80 psig to about 240 psig and at temperatures of about 100°F. Liquid product is removed from separator **33** through line **34** to be sent to a suitable product recovery system from which a high-octane-number product is obtained. Gaseous material is removed from the separator **33** through line **35.** A portion of this gas is removed from the system through line **36** to be used at other refinery units. The remainder of the hydrogen-hydrocarbon gas in line **35** is compressed by compressor **37** to be sent through lines **38** and **14** as hydrogen-hydrocarbon recycle gas. When necessary, make-up hydrogen gas may be introduced into the system from source **39** via line **40.**

The above-described preferred embodiment and the following examples are presented herein to facilitate the understanding of the present invention. These are presented for the purpose of illustration only and are not intended to limit the scope of the present invention.

EXAMPLE I

Representative samples of two commercially-prepared reforming catalysts were obtained from the American Cyanamid Company. The first of these, hereinafter identified as Catalyst A, contained 0.74 wt.%

platinum and 0.77 wt.% chloride on a gamma-alumina. The second, hereinafter identified as Catalyst B, contained 0.56 wt.% platinum, 0.51 wt.% rhenium, and 0.79 wt.% chloride on a gamma-alumina support.

Catalyst C was prepared in the laboratory to contain 1 wt.% gallium, based upon the total weight of the catalytic composition. A 50-gram sample of Catalyst A was impregnated with 50 cc of a solution that had been prepared by dissolving 3 grams of gallium nitrate, $Ga(NO_3)_3 \cdot 9H_2O$ in distilled water. The impregnated material was then dried in air at 250°F. and subsequently calcined in air at 1,000°F. For this catalyst preparation and for those described hereinafter, the material to be impregnated had been pulverized to a 20-to-40-mesh material, that is, the material was of a particle size that would pass through a 20-mesh screen but would be retained upon a 40-mesh screen (U.S. Sieve Series). Unless otherwise stated, for each catalyst preparation described herein, the drying and calcining were carried out in flowing air at an air rate of 1.5 cubic feet per hour. The drying and calcining were each conducted for three hours. Catalyst C was found to contain 0.34 wt.% chloride.

Catalyst D was prepared in the laboratory to contain 1 wt.% gallium. A 50-gram portion of a commercially-prepared reforming catalyst, obtained from the American Cyanamid Company and containing 0.43 wt.% platinum and 0.42 wt.% chloride on a gamma-alumina, was impregnated with 50 cc of a solution of gallium nitrate. This solution had been prepared by dissolving 3 grams of gallium nitrate in distilled water. The impregnated material was dried and calcined. Catalyst D contained 0.30 wt.% chloride.

Catalyst E was prepared to contain 1 wt.% gallium. A 50-gram portion of the commercially-prepared catalyst that was employed in the preparation of Catalyst D was impregnated with a solution that had been prepared by dissolving 3 grams of gallium nitrate and 1.345 grams of 37.5% hydrochloric acid in 50 ml. of distilled water. The impregnated material was dried and calcined. Catalyst E was found to contain 0.61 wt.% chloride.

EXAMPLE II

Each of the catalysts that was prepared or obtained in Example I was tested for its ability to reform a partially-reformed naphtha. The various properties of this feedstock are presented hereinbelow in Table I.

TABLE I

FEEDSTOCK PROPERTIES

Gravity, °API	48.9
Specific Gravity	0.7844
Research Octane No.	87.4
ASTM Distillation, °F.	
IBP	118
10%	188
30	230
50	256
70	284
90	324
FBP	398
Composition, Vol.%	
Paraffins	43.8
Naphthenes	3.0
Aromatics	53.2
Sulfur, ppm	0.3
Nitrogen, ppm	0.4

The testing was carried out in a bench-scale test unit employing an isothermal fixed bed of catalyst. The hydrocarbon feedstock and bottled hydrogen (once-through) were mixed and the resulting hydrogen-hydrocarbon mixture was charged to a reactor having an inside diameter of 0.622 inch. The reactor, which was 20 inches long, was immersed in a heating bath containing DuPont HITEC. The hydrocarbon feed was pumped by a positive-displacement Ruska pump. The effluent from the reactor was sent to conventional product handling and recovery equipment. Liquid samples for octane analysis were collected overnight (for 17 hours) at ambient temperature. Material balances were obtained from samples collected for one hour with a dry ice knock-back and such samples were analyzed by gas chromatographic techniques.

Each catalyst sample that was charged to the reactor was in the form of 20–40-mesh material (U.S. Sieve Series). After the reactor was placed in the test unit, the catalyst was pretreated by being subjected to an air soak for one-half hour at an air rate of about 2 cubic feet per hour, a temperature of about 900°F., and a pressure of 200 psig. Subsequently, the catalyst was purged with nitrogen and then reduced with hydrogen for one hour at the test temperature and pressure. For the catalyst containing rhenium, Catalyst B, a presulfiding technique was also employed. This catalyst was pre-sulfided with a gas mixture of 8 volume percent hydrogen sulfide in hydrogen at test temperature and pressure before the catalyst was tested. These tests were conducted at a pressure of 200 psig, a WHSV of 3.62, a kinetic average temperature of about 900°F., and a hydrogen addition rate of about 3,000 SCFB. In each case, 13 grams of catalyst were employed. When the unit was placed on test, no sampling was performed for the first 5 hours to permit the test to line out.

The test results are presented in FIG. 2. The unleaded C^+_5 research octane numbers which were obtained in the tests were corrected to a temperature of 900°F. and to an initial chloride level on the catalyst of 0.74 wt.% chloride. These corrections were made by use of emperical correlations. Please note that the average performance of the catalysts that were promoted with gallium is represented by a solid line, while the performances of each of those catalysts are represented by broken lines. The difference in platinum level between two catalysts would not appreciably affect the performances of the two catalysts.

The results in FIG. 2 show that those tests which employed Catalysts C, D, and E, i.e., embodiments of the process of the present invention, provided C^+_5 research octane numbers that were far superior to those tests which employed Catalysts A and B. Those two tests employing Catalysts A and B represented prior-art reforming processes. The C^+_5 liquid yield data obtained from these tests in this bench-scale unit did not provide sufficient differences between the tests to distinguish the yields obtained with one catalyst from those obtained with another.

What is claimed is:

1. A process for the reforming of a petroleum hydrocarbon stream, which process comprises contacting said hydrocarbon stream in a first reforming zone under reforming conditions and in the presence of hydrogen with a first reforming catalyst consisting essentially of a member selected from the group consisting of a Group VI metal of the Periodic Table of Elements, oxides of a Group VI metal, and a Group VIII noble metal as a hydrogenation component, a catalytically active alumina, and, when a Group VIII noble metal is

the hydrogenation component, about 0.5 wt.% to about 2 wt.% halide and 0 wt.% to about 2 wt.% rhenium to produce a first reformate and subsequently contacting said first reformate in a second reforming zone under reforming conditions and in the presence of hydrogen with a second reforming catalyst comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide, said hydrogenation component of said second reforming catalyst being a member selected from the group consisting of a Group VI metal of the Periodic Table of Elements, oxides of a Group VI metal, and a Group VIII noble metal, and said small amount of gallium being within the range of about 0.05 wt.% to about 3 wt.%, calculated as the element and based upon the total weight of said second reforming catalyst.

2. The process of claim **1** wherein said hydrogenation component of said first reforming catalyst is a Group VIII noble metal and is present in an amount of about 0.1 wt.% to about 2 wt.%.

3. The process of claim **1** wherein said porous refractory inorganic oxide of said second reforming catalyst is a catalytically active alumina.

4. The process of claim **1** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

5. The process of claim **1** wherein said petroleum hydrocarbon stream comprises a member selected from the group consisting of a virgin naphtha, a cracked naphtha, a partially-reformed naphtha, a hydrocarbon fraction boiling in the gasoline boiling range, and mixtures thereof.

6. The process of claim **1** wherein said hydrogenation component of said second reforming catalyst comprises a Group VIII noble metal and is present in an amount of about 0.05 wt.% to about 2 wt.%, calculated as the element and based upon the total weight of said second reforming catalyst.

7. The process of claim **1** wherein said second reforming catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said second reforming catalyst.

8. The process of claim **2** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

9. The process of claim **2** wherein said porous refractory inorganic oxide of said second reforming catalyst is a catalytically active alumina.

10. The process of claim **2** wherein said petroleum hydrocarbon stream comprises a member selected from the group consisting of a virgin naphtha, a cracked naphtha, a partially-reformed naphtha, a hydrocarbon fraction boiling in the gasoline boiling range, and mixtures thereof.

11. The process of claim **3** wherein said hydrogenation component of said second reforming catalyst comprises a Group VIII noble metal and is present in an amount of about 0.05 wt.% to about 2 wt.%, calculated as the element and based upon the total weight of said second reforming catalyst.

12. The process of claim **3** wherein said second reforming catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said second reforming catalyst.

13. The process of claim **5** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

14. The process of claim **8** wherein said petroleum hydrocarbon stream comprises a member selected from the group consisting of a virgin naphtha, a cracked naphtha, a partially-reformed naphtha, a hydrocarbon fraction boiling in the gasoline boiling range, and mixtures thereof.

15. The process of claim **9** wherein said hydrogenation component of said second reforming catalyst comprises a Group VIII noble metal and is present in an amount of about 0.05 wt.% to about 2 wt.%, calculated as the element and based upon the total weight of said second reforming catalyst.

16. The process of claim **11** wherein said Group VIII noble metal of said second reforming catalyst is platinum and wherein said second reforming catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said second reforming catalyst.

17. The process of claim **15** wherein said Group VIII noble metal of said second reforming catalyst is platinum and wherein said second reforming catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said second reforming catalyst.

18. The process of claim **16** wherein said halide is chloride.

19. The process of claim **17** wherein said halide of said second reforming catalyst is chloride.

20. The process of claim **18** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

21. The process of claim **20** wherein said petroleum hydrocarbon stream comprises a member selected from the group consisting of a virgin naphtha, a cracked naphtha, a partially-reformed naphtha, a hydrocarbon fraction boiling in the gasoline boiling range, and mixtures thereof.

22. The process of claim **19** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

23. The process of claim **22** wherein said petroleum hydrocarbon stream comprises a member selected from the group consisting of a virgin naphtha, a cracked naphtha, a partially-reformed naphtha, a hydrocarbon fraction boiling in the gasoline boiling range, and mixtures thereof.

24. A process for reforming a partially-reformed hydrocarbon stream, which process comprises contacting said hydrocarbon stream in a reforming zone under reforming conditions and in the presence of hydrogen with a catalyst comprising a hydrogenation component and a small amount of gallium on a solid catalytic support comprising a porous refractory inorganic oxide, said hydrogenation component of said catalyst being a member selected from the group consisting of a Group VI metal of the Periodic Table of Elements, oxides of a Group VI metal, and a Group VIII noble metal, and said small amount of gallium being within the range of about 0.05 wt.% to about 3 wt.%, calculated as the element and based upon the total weight of said catalyst.

25. The process of claim **24** wherein said porous refractory inorganic oxide comprises a catalytically active alumina.

26. The process of claim **24** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

27. The process of claim **24** wherein said hydrogenation component of said catalyst comprises a Group VIII noble metal and is present in an amount of about 0.05 wt.% to about 2 wt.%, calculated as the element and based upon the total weight of said catalyst.

28. The process of claim **24** wherein said catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said catalyst.

29. The process of claim **25** wherein said hydrogenation component of said catalyst comprises a Group VIII noble metal and is present in an amount of about 0.05 wt.% to about 2 wt.%, calculated as the element and based upon the total weight of said catalyst.

30. The process of claim **25** wherein said catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said catalyst.

31. The process of claim **30** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

32. The process of claim **29** wherein said catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said catalyst.

33. The process of claim **29** wherein said Group VIII noble metal of said catalyst is platinum.

34. The process of claim **32** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

35. The process of claim **33** wherein said catalyst also contains a halide, said halide being present in an amount of about 0.1 wt.% to about 2 wt.%, based upon the total weight of said catalyst.

36. The process of claim **35** wherein said halide of said catalyst is chloride.

37. The process of claim **35** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

38. The process of claim **36** wherein said reforming conditions comprise an average catalyst temperature of about 700°F. to about 1,050°F., a pressure of about 50 psig to about 1,000 psig, a WHSV of about 0.5 to about 15 weight units of hydrocarbon per hour per weight unit of catalyst, and a hydrogen addition rate of about 1,500 SCFB to about 15,000 SCFB.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,772,183 Dated November 13, 1973

Inventor(s) Ralph J. Bertolacini and Dae K. Kim

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 57, "gallim" should be -- gallium --.

Column 6, line 12, "(SCFG)" should be -- (SCFB) --.

Column 7, line 7, "process" should be -- system --.

Signed and sealed this 9th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents