Aug. 20, 1974 H. E. KLUKSDAHL ET AL 3,830,727

REFORMING PROCESS WITH PROMOTED CATALYST

Original Filed Jan. 30, 1970 2 Sheets-Sheet 1

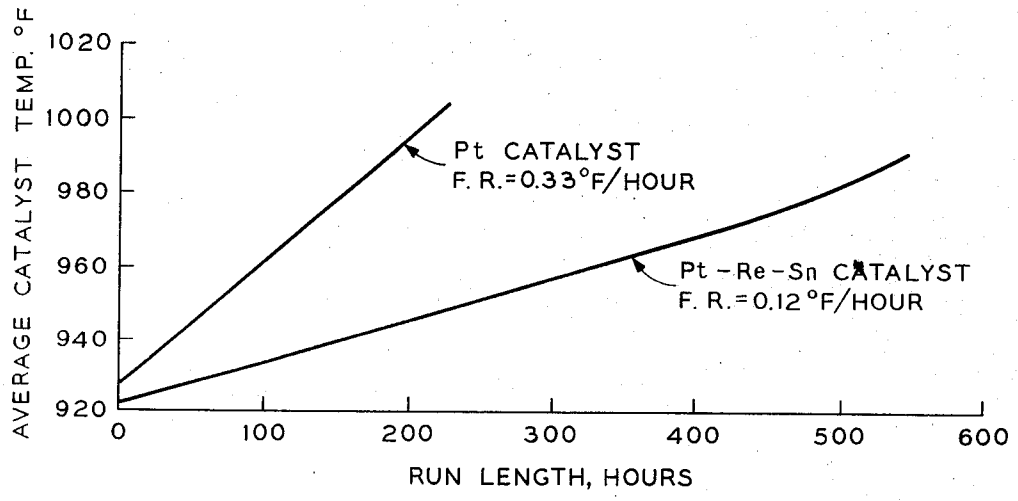


FIG. 1

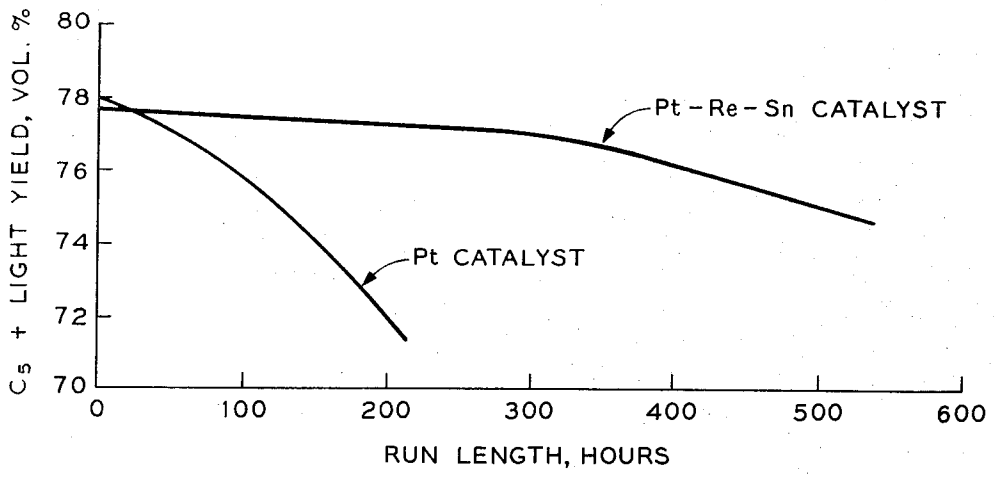


FIG. 2

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REFORMING PROCESS WITH PROMOTED CATALYST

Original Filed Jan. 30, 1970 2 Sheets-Sheet 2

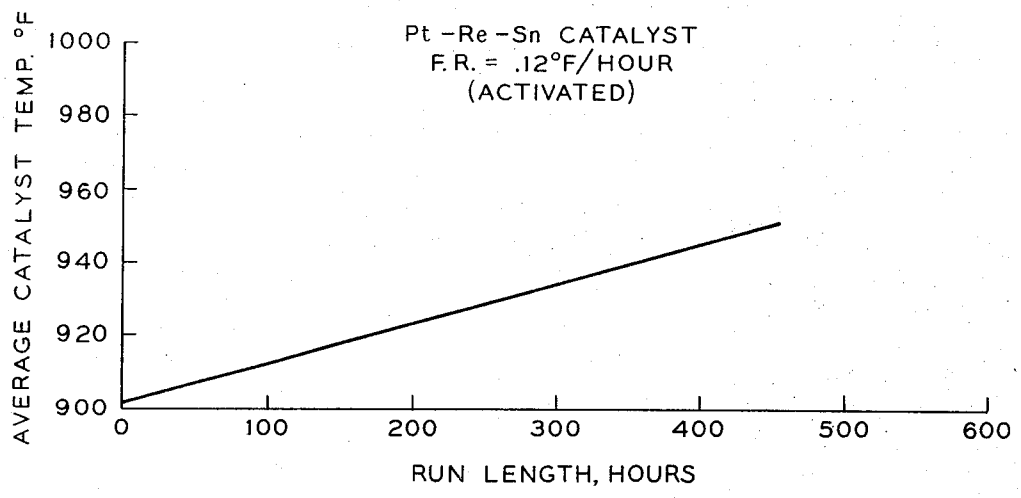


FIG. 3

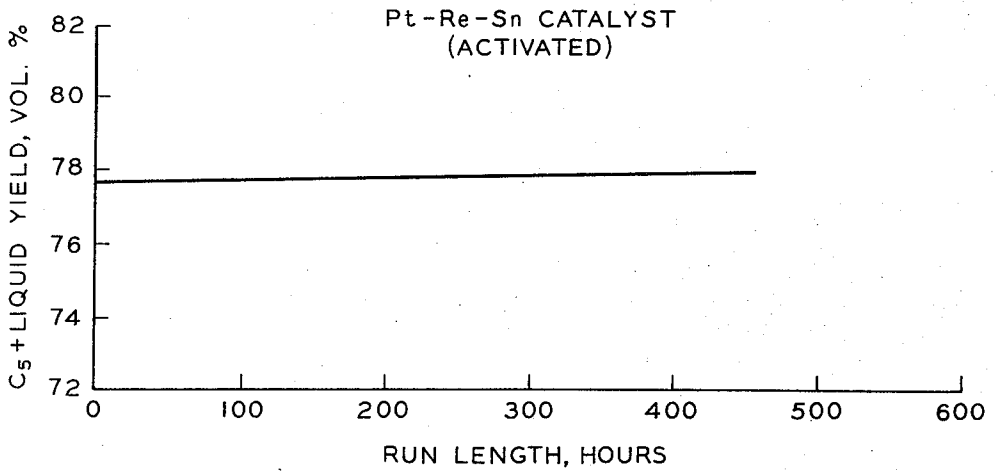


FIG. 4

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REFORMING PROCESS WITH PROMOTED CATALYST

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Continuation of abandoned application Ser. No. 7,061, Jan. 30, 1970. This application June 16, 1972, Ser. No. 263,574

Int. Cl. C10g 35/08

U.S. Cl. 208—139 3 Claims

ABSTRACT OF THE DISCLOSURE

Process for reforming a naphtha feedstock, comprising: contacting a naphtha feedstock containing less than about 10 p.p.m. by weight sulfur and less than about 50 p.p.m. by weight water, at reforming conditions and in the presence of hydrogen with a catalytic composition including a porous alumina-containing solid carrier, 0.01 to 3 weight percent platinum, 0.01 to 3 weight precent rhenium, 0.01 to 8 weight percent tin, and 0.1 to 3 weight percent halogen wherein the catalytic composition prior to the contacting is activated by the step comprising reacting the catalytic composition with an activating gas including oxygen and a halogenating component at a temperature from 500° F. to 1300° F. for at least about 0.5 hours.

This is a continuation of application Ser. No. 7,061, filed Jan. 30, 1970, now abandoned.

BACKGROUND

This invention relates to hydrocarbon reforming processes and more particularly to catalytic reforming of a naphtha fraction in the presence of a novel catalyst comprising a porous solid carrier, platinum, rhenium, and tin. The catalyst comprises 0.01 to 3 weight percent platinum, 0.01 to 3 weight percent rhenium, 0.01 to 2 weight percent tin and a porous solid carrier.

Catalytic reforming is well known in the petroleum industry and refers to the treatment of naphtha feedstocks to improve the octane rating, primarily through increasing the aromatic content thereof, for example by dehydrogenating naphthenes to aromatics, dehydrocyclizing paraffins to naphthenes and aromatics, and the like. Catalysts for successful reforming processes should possess good selectivity, that is, be able to produce high yields of high octane number gasoline products and, accordingly, low yields of light gaseous hydrocarbons or carbonaceous by-products. In addition, it is very desirable that the catalysts exhibit good yield stability; that is, the yield of C_5+ gasoline product of a certain octane number should not decrease appreciably during the prolonged period of reforming. Decreases in C_5+ liquid yield of only a few percent during the process represent a substantial economic loss. Another characteristic of good reforming catalysts is a low fouling rate; that is, the rate of increase in temperature necessary to maintain conversion of the feed to constant octane number gasoline product should be relatively low. Rapid fouling of the catalyst requires early shutdown of the reforming process and subsequent regeneration of the catalysts.

Catalysts comprising platinum, for example, platinum supported on alumina, are well known and widely used for the reforming of naphthas and gasoline boiling range materials in order to produce high octane gasolines. Platinum catalysts are highly selective towards the production of high octane aromatics and highly active for the several reactions during reforming. However, platinum catalysts are also very expensive due to the high cost of platinum and will probably become even more expensive as a result of the restricted availability of the metal.

In U.S. Pat. No. 3,415,737, a catalyst composition comprising platinum and rhenium in association with a carrier, for example, alumina, is disclosed as being highly useful for reforming processes. The platinum-rhenium catalytic composite has enhanced yield stability and a low fouling rate compared to a catalyst comprising platinum without rhenium. While rhenium is significantly less expensive than platinum, it is still a relatively expensive metal. Furthermore, rhenium is in very short supply. In general, as the concentrations of platinum and rhenium in a platinum-rhenium catalyst decrease, the fouling rate of the catalyst increases in comparison to catalytic composites comprising higher concentrations of platinum and rhenium.

In my recent application, Ser. No. 865,010, filed Oct. 9, 1969, a catalyst composition comprising platinum and tin in association with a carrier is disclosed as exhibiting a remarkably low fouling rate as compared to a catalyst comprising platinum without tin in association with a carrier. The platinum-tin catalyst also yield stability better than that of a platinum catalyst without tin. In general, as the concentrations of platinum and tin in a platinum-tin catalyst decrease, the fouling rate of the catalyst increases in comparison to catalytic composites comprising higher concentrations of platinum and tin.

SUMMARY OF THE INVENTION

It has now been discovered that catalyst compositions comprising platinum, rhenium, and tin, that is, from 0.01 to 3.0 weight percent platinum, 0.01 to 3.0 weight percent rhenium, and 0.01 to 8 weight percent tin, included with a porous solid carrier, result in a catalyst having unexpectedly high yield stability and low fouling rate. Desirable benefits of platinum-rhenium catalysts are retained at lowered rhenium levels.

The process of the present invention comprises contacting a naphtha fraction and hydrogen at reforming conditions with a catalyst composition including a porous solid carrier, 0.01 to 3 weight percent platinum, 0.01 to 3 weight percent rhenium, and 0.01 to 8 weight percent tin. Preferably the porous solid carrier is an inorganic oxide, more preferably alumina.

Furthermore, the present invention comprises the novel catalytic composition including a porous solid carrier, 0.01 to 3 weight percent platinum, 0.01 to 3 weight percent rhenium, and 0.01 to 8 weight percent tin.

DESCRIPTION OF THE DRAWINGS

The present invention can be better understood and will be further explained hereinafter with reference to the graphs in FIGS. 1–4.

The graphs in FIGS. 1 and 2 show, for comparison purposes, data from simulated life tests indicating the reforming activity and stability of a conventional catalyst comprising 0.3 weight percent platinum on an alumina support and a catalyst comprising 0.3 weight percent platinum, 0.1 weight percent rhenium and 0.2 weight percent tin on an alumina support. Conditions of operation, as defined below, were more severe than normally used in reforming operations. The graph in FIG. 1 shows the average catalyst temperature as a function of the length of the test or hours on stream required to maintain a 102 F–1 clear octane product for each of the two catalysts. The graph in FIG. 2 shows as a function of the time on-stream the yield of C_5+ liquid product or gasoline having 102 F–1 clear octane rating produced during the reforming using each of the two catalysts. The conditions of operation for the reforming process using each catalyst included a pressure of 200 p.s.i.g., a hydrogen to hydrocarbon mole ratio of 6 and a liquid hourly space velocity of 2. The catalyst comprising platinum without tin and rhenium exhibited relatively rapid fouling. From FIG. 1 it is seen that the platinum-rhenium-tin catalyst

fouls at a much lower rate than the platinum catalyst without tin and rhenium. From FIG. 2 it is seen that the process using the platinum-rhenium-tin catalyst yields significantly higher amounts of 102 F-1 clear octane product that the process using the platinum catalyst without tin and rhenium.

The graphs in FIGS. 3 and 4 show data from a simulated life test indicating the activity of a catalyst comprising 0.3 weight percent platinum, 0.4 weight percent rhenium, and 1.4 weight percent combined halogen. The catalyst was activated by being calcined at 950° F. in an air-nitrogen mixture containing about 5 weight percent oxygen. The halogen content of the catalyst was raised from a pre-activation value of 1.2 weight percent to 1.4 weight percent by including a halogenating component, namely, carbon tetrachloride, with the air-nitrogen mixture during the activation. Conditions of operation were identical to those used in the processes shown in FIGS. 1 and 2. FIGS 3 and 4 indicate that an activated platinum-rhenium-tin catalyst having a halogen content of 1.4 weight percent has a very low fouling rate and very good yield stability.

DESCRIPTION OF THE INVENTION

The Catalytic Composition

The porous solid carrier or support that is employed in the preparation of the catalytic composition of the present invention includes a large number of materials with which catalytically active amounts of platinum, rhenium, and tin can be included. The porous solid carrier can be, for example, charcoal or carbon. A high surface area inorganic oxide carrier is particularly preferred, e.g., an inorganic oxide having a surface area of from 50–700 $m.^2/gm$. The carrier can be a natural or a synthetically-produced inorganic oxide or combination of inorganic oxides. Typical acidic inorganic oxide supports which can be used are the naturally occurring aluminum silicates and the synthetically-produced cracking supports, such as silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, and crystalline zeolitic aluminosilicates. Generally, reforming processes are preferably conducted in the presence of catalysts having low cracking activity, i.e., catalysts of limited acidity. Hence, preferred carriers are inorganic oxides such as magnesia and alumina, particularly high purity alumina.

A particularly preferred catalytic carrier or support for purposes of this invention is alumina. Any of the forms of alumina suitable as a carrier for reforming catalysts can be used. Furthermore, alumina can be prepared by a variety of methods satisfactory for the purposes of this invention. The preparation of alumina for use in reforming catalysts is well known in the prior art. Thus, the alumina may be prepared as alumina hydrosol, alumina hydrogel, alumina zerogel, alumina monohydrate, sintered alumina, and the like.

The catalytic composition includes a porous solid carrier, and catalytically active amounts of platinum, rhenium, and tin, preferably in intimate admixture. The catalyst proposed for use in the present invention comprises platinum in amounts of from 0.01 to 3 weight percent and more preferably from 0.01 to 1.0 weight percent based on the finished catalyst. The concentration of rhenium in the final composition is from 0.01 to 3 weight percent and preferably from 0.01 to 1.0 weight percent. The tin concentration in the finished catalyst composition is from 0.01 to 8 weight percent, preferably from 0.01 to 5 weight percent, and more preferably from 0.01 to 1.0 weight percent. The platinum, rhenium, and tin may exist as metals or as compounds on the finished catalyst. Reference to "platinum," "rhenium" and "tin" is meant to include the metallic form as well as the compound form, e.g., the sulfide, halide, or oxide form. The weight percent of the platinum, rhenium, and tin is calculated on the basis of the metal.

Although the components, platinum, rhenium, and tin can be included with the porous solid carrier by any suitable technique such as ion-exchange, coprecipitation, etc., the components are usually and preferably included with the porous solid carrier by impregnation. One of the components can be included with the carrier by one procedure, e.g., ion exchange, and the other components included with the carrier by another procedure, e.g., impregnation. The catalyst can be prepared either by coimpregnation of the three components or by sequential impregnation. In general, the carrier material is impregnated with a solution of a decomposable compound of the metal in sufficient concentration to provide the desired quantity of metal in the finished catalyst; the resulting mixture is then heated to remove solvent. Chloroplatinic acid in an aqueous solution is generally the preferred source of platinum. Other feasible platinum-containing compounds, e.g., ammonium chloroplatinates and polyamine platinum salts, can also be used. Rhenium compounds suitable for including onto the carrier include, among others perrhenic acid and ammonium perrhenates in aqueous solution. Tin compounds suitable for including onto the carrier include stannous chloride, stannic chloride, other tin halides, organic tin derivatives, and other tin containing salts.

The tin component is preferably associated with the porous solid carrier suitably by impregnation. Impregnation can be accomplished using an aqueous solution of a suitable compound. When using an aqueous tin impregnating procedure, it may be desirable to activate the resulting catalytic composition of matter so that it will exhibit optimum catalytic activity. The preferred activation process comprises reacting the catalytic composition with an activating gas including oxygen at a temperature from 500° F. to 1300° F. for at least about 0.5 hour. The activating gas may be slightly moist. The activating gas may preferably include a halogenating component and if it includes a halogenating component it is preferably slightly moist.

As another embodiment, the tin component is impregnated on the carrier from an organic solution. Thus a tin compound dissolved in ether or alcohol or other suitable organic solvent may be used as the impregnation solution. Care should be exercised after impregnation that the organic material is completely evaporated or removed from the catalyst prior to heating of the catalyst in the presence of a reducing atmosphere, for example, hydrogen. Thus, careful drying or calcination should follow impregnation using an organic solvent in order to thoroughly rid the catalyst of hydrocarbon molecules. The presence of hydrocarbons on the catalyst during contact with a hydrogen atmosphere appears to detrimentally affect the performance of the catalyst during hydroconversion reactions as, for example, reforming. The organic solution is preferably substantially anhydrous. If it is not substantially anhydrous, then the catalytic composition should preferably be activated as described above so that it has substantially optimum activity. In general, if the catalytic composition is contacted with a substantial amount of moisture during or after impregnation with a tin component, it is desirable to activate the composition by the disclosed process so that it will have substantially optimum activity.

It is contemplated in the present invention that including of the components, platinum, rhenium, and tin, with the carrier can be accomplished at any particular stage of the catalyst preparation. For example, if the components are to be included with an alumina support, the including may take place while the alumina is in the sol or gel form followed by precipitation of the alumina. Alternatively, a previously prepared alumina carrier can be impregnated with a solution of the metal compounds.

Following inclusion of the carrier material with platinum, rhenium, and tin, the resulting composition is usually dried by heating at a temperature of, for example, no

greater than about 500° F. and preferably at about 200° F. to 400° F. Thereafter the composition can be calcined in an oxygen-containing atmosphere, e.g., air, at an elevated temperature, e.g., up to about 1300° F., if desired. It may be desirable to include one or two components, for example, platinum and/or rhenium, with the carrier, followed by drying and calcination, before including the other component or components.

The carrier containing 0.01 to 3 weight percent platinum, 0.01 to 3 weight percent rhenium, and 0.01 to 8 weight percent tin is preferably heated at an elevated temperature in a hydrogen-containing atmosphere. Preferably the heating is performed in the presence of a substantially hydrocarbon-free, hydrogen containing gas that is also substantially free of carbon oxides and water. More preferably, the gas is substantially dry hydrogen. In particular, it is preferred that this heating is accomplished at a temperature in the range of 600° F. to 1300° F. and preferably 600° F. to 1000° F.

The catalyst can be promoted for reforming by the inclusion of combined halogens (halides), particularly fluorine or chlorine. Bromine is also useful for promoting the catalyst for reforming. The halogens apparently provide a limited amount of acidity to the catalyst which is beneficial to most reforming operations. A catalyst promoted with halogen preferably contains from 0.1 to 3 weight percent, more preferably 0.5 to 2.0 weight percent, and still more preferably 0.8 to 1.6 weight percent, total halogen content. The halogen can be included with the catalyst carrier at any suitable stage of catalyst manufacture, e.g., prior to or following inclusion of the platinum, rhenium, or tin. Some halogen is often included with the carrier when impregnating with the metal components; for example, impregnation with chloroplatinic acid normally results in chlorine inclusion with the carrier. Additional halogen may be included with the support simultaneously with the inclusion of the metal component if so desired. If the catalyst is activated, as previously described, some halogen can be incorporated during the activation. Halogen can also be included with the catalyst during startup and/or reforming. Including of halogen can be accomplished by passing a gas containing a halogenating component, for example, carbon tetrachloride, chloroform, and the like, in contact with the catalyst at a temperature sufficient to cause reaction, e.g., 600–1300° F. The halogen conent of the catalyst can be adjusted during the reforming by adding a halogenating component to the reaction zone with the feed, hydrogen, or feed-hydrogen mixture. In general, the halogen is included with the catalyst carrier by contacting suitable compounds such as hydrogen fluoride, ammonium fluoride, hydrogen chloride, or ammonium chloride, either in the gaseous form or in a water soluble form, with the carrier. Preferably, the halogen is included with the carrier from an aqueous solution containing the halogen.

The catalyst can be sulfided prior to contact with the feed in the reaction zone. Sulfiding the catalyst prior to contact with the naphtha helps reduce the production of light hydrocarbon gases during startup. The presulfiding can be done in situ or ex situ by passing a sulfur-containing gas, for example, H_2S, in the presence of hydrogen, over the catalyst. Other presulfiding treatments are known in the prior art. Also, it has been found that on startup a small amount of sulfur, for example, H_2S or dimethyldisulfide, added to the reforming zone with the feed, may help to reduce the initial hydrocracking activity of the catalyst. The sulfur can be introduced in any convenient manner and at any convenient location. It can be contained in the liquid hydrocarbon feed, the hydrogen-rich gas, a recycle liquid stream, or a recycle gas stream or any combination. Generally, during the reforming process most sulfur contained on the catalyst is stripped from the catalyst and will thus be removed from the reaction zone.

Feedstock

The feedstock to be employed in the reforming operation is a light hydrocarbon oil, for example, a naphtha fraction, i.e., a mixture of aromatic, paraffinic, and naphthenic hydrocarbons. Generally, the naphtha will boil in the range falling within the limits of from 70 to 550° F. and preferably 150 to 450° F. The feedstock can be a straight-run naphtha, a thermally or catalytically cracked naphtha, a hydrocracked naphtha, or blends or fractions thereof. Preferably the feed should be substantially free of sulfur, that is, the feed should preferably contain less than about 10 p.p.m. sulfur, more preferably less than 5 p.p.m. sulfur, and still more preferably less than 1 p.p.m. sulfur. The sulfur content is determined as weight of sulfur to weight of feed.

In the case of a feedstock which is not already low in sulfur, lower levels can be reached by hydrogenating the feedstock in a presaturation zone where the naphtha is contacted with a hydrogenation catalyst which is resistant to sulfur poisoning. A suitable catalyst for this hydrodesulfurization process is, for example, an alumina-containing support with a minor proportion of molybdenum oxide and cobalt oxide. Hydrodrodesulfurization is ordinarily conducted at a temperature from 700 to 850° F., a pressure from 200 to 2000 p.s.i.g., and a liquid hourly space velocity from 1 to 5. The sulfur contained in the naphtha is converted to hydrogen sulfide which can be removed prior to reforming by suitable conventional processes.

It is preferred that the feed be substantially free of moisture, that is, the feed should preferably contain less than about 50 p.p.m. water, more preferably less than 15 p.p.m. water. This serves to keep the activtiy of the catalyst high for longer periods of time.

In the case of a reforming process wherein the effluent is separated into reformed gasoline product and hydrogen-rich gas and the hydrogen-rich gas is recycled to the gas zone, it may be desirable to pass the hydrogen-rich gas in contact with an adsorption zone, for example, a molecular sieve, to remove sulfur from the recycle stream. Also the absorption zone will remove water from the recycle stream. Thus, the concentration of impurities, for example, sulfur and water, will not be permitted to build up to significant amounts in the recycle stream. However, it is understood that it is not essential that the sulfur be scrubbed from the recycle stream.

Reforming Conditions

The reforming conditions used in the present invention will depend in large measure on the feed used, whether highly aromatic, paraffinic, or naphthenic, and upon the desired octane rating of the product. The temperature in the reforming operation will generally be in the range of about 500 to 1300° F. and preferably about 700 to 1050° F. The pressure in the reforming reaction will in general lie within the range from about 25 to 1000 p.s.i.g., and preferably from about 50 to 750 p.s.i.g. The temperature and pressure can be correlated with the liquid hourly space velocity (LHSV) to favor any particularly desirable reforming reaction as, for example, aromatization or isomerization or dehydrogenation. In general, the liquid hourly space velocity will be from 0.1 to 20 and preferably from 1 to 10.

Reforming of a naphtha is accomplished by contacting the naphtha at reforming conditions and in the presence of hydrogen with the desired catalyst. Reforming generally results in the production of hydrogen. The hydrogen produced during the reforming process is generally recovered from the reaction products, and, preferably, at least part of said hydrogen is recycled to the reaction zone. Thus, excess hydrogen need not necessarily be added to the reforming system. However, it is usually preferred to introduce excess hydrogen at some stage during the operation as, for example, during startup. The hydrogen can be intro-

duced into the feed prior to contact with the catalyst or can be contacted simultaneously with the introduction of the feed to the reaction zone. Generally, the hydrogen is recirculated over the catalyst prior to contact of the feed with the catalyst. The presence of hydrogen serves to reduce the formation of coke which tends to poison the catalyst. Moreover, the presence of hydrogen can be used to favor certain reforming reactions, e.g., isomerization, or hydrocracking. Hydrogen is perferably introduced into the reforming reactor at a rate in the range from about 0.5 to about 20 moles of hydrogen per mole of feed. The hydrogen can be in admixture with light gaseous hydrocarbons.

Regeneration

After a period of operation when the catalyst becomes deactivated by the presence of carbonaceous deposits, the catalyst can be regenerated by passing an oxygen-containing gas, such as air diluted with an inert gas to contain no more than about 2% oxygen, into contact with the catalysts at an elevated temperature in order to burn carbonaceous deposits from the catalyst. The method of regenerating the catalyst will depend on whether there is a fixed bed, moving bed, or fluidized bed operation. Regeneration methods and conditions well known in the art can be used.

It may also be desirable to activate the catalyst after it is regenerated. This may be accomplished in precisely the manner previously disclosed for activatig a fresh platinum-rhenium-tin catalyst wherein the tin has been included with the catalyst by impregnation with an aqueous solution. The use of a halogenating component included with the activating gas is generally attractive when activating a deactivated catalyst since the catalyst may have lost some halogen during its use in the reforming process. Halogen analysis of the catalyst can be performed to determine whether a halogenating component should be included with the activating gas.

After regeneration, or regeneration and activation if the catalyst is activated, the catalyst is preferably heated at an elevated temperature in a hydrogen containing atmosphere. Preferably, the heating is performed in the presence of a substantially hydrocarbon-free, hydrogen containing gas that is preferably substantially dry and substantially free of carbon oxides at a temperature from 600° F. to 1300° F., and more preferably from 600° F. to 1000° F.

The process of the present invention will be more readily understood by reference to the following Examples. The Examples are illustrative only and the invention, of course, is not to be limited thereto.

Example 1

Catalysts A, B and C were each individually used in reforming a hydrofined catalytically cracked naphtha under accelerated conditions. Catalyst A comprised 0.3 weight percent platinum, 0.1 weight percent rhenium, and 0.6 weight percent chlorine. Catalyst B comprised 0.3 weight percent platinum, 0.2 weight percent tin, and 0.7 weight percent chlorine. Catalyst C comprised 0.3 weight percent platinum, 0.1 weight percent rhenium, 0.2 weight percent tin, and 0.7 weight percent chlorine. The processes were conducted at reforming conditions including an average reactor pressure of 125 p.s.i.g., a hydrogen to hydrocarbon mole ratio of 3 and a liquid hourly space velocity of 3. The temperature of the catalyst, in the process using each catalyst, was adjusted throughout each run to maintain production of a 100 F–1 clear octane product. The runs were made using once-through hydrogen. The hydrofined catalytically cracked naphtha had an initial boiling point of 151° F., an end boiling point of 428° F. and a 50 percent boiling point of 307° F. The research octane number of the feed without anti-knock additives (F–1 clear) was 64.6. The naphtha contained less than 0.1 p.p.m. nitrogen and less than 0.1 p.p.m. sulfur. The feed was specifically chosen because of its severe deactivating effect upon reforming catalyst. Using this feed and the above reaction conditions, tests of reforming catalysts can be accelerated, i.e., performed in a fraction of the time needed with a less severely deactivating feed and under less severe conditions.

The results of reforming the naphtha at the accelerated conditions specified, using Catalysts A, B, and C, are shown in Tables I and II. The data in Table I show the starting temperature in degrees Fahrenheit and the fouling rate in degrees Fahrenheit per hour. The data in Table II, show the C_5+ yield at the start of the run and after 20 hours on stream.

TABLE I

	Catalyst composition				Starting temperature	Fouling rate, ° F./hour
	Pt	Re	Sn	Cl		
A	0.3	0.1	-------	0.6	918	2.55
B	0.3	-------	0.2	0.7	899	1.9
C	0.3	0.1	0.2	0.7	905	1.9

TABLE II

	Catalyst composition				C_5+ liquid yield, volume percent	
	Pt	Re	Sn	Cl	Initial	At 20 hours
A	0.3	0.1	-------	0.6	85.4	82.8
B	0.3	-------	0.2	0.7	85.7	85.0
C	0.3	0.1	0.2	0.7	85.8	85.3

The yield of C_5+ product obtained using Catalyst C remained high over the entire run length. The reforming periods were of substantial duration considering the low pressure and accelerated nature of the test.

Example 2

Reforming processes using (1) Catalyst C, and (2) a catalyst comprising 0.3 weight percent platinum on an alumina support without tin (Catalyst D) were compared. Both catalysts were used in the reforming of a naphtha feed. The naphtha feed was a hydrofined catalytically cracked naphtha having an initial boiling point of 196° F., and end boiling point of 378° F. and a 50 percent boiling point of 268° F. It contained 39.8 volume percent paraffins, 48.3 volume percent naphthas, and 11.9 volume percent aromatics. It contained less than 0.1 p.p.m. nitrogen and less than 0.1 p.p.m. sulfur.

The reforming was performed at a pressure of 200 p.s.i.g., a liquid hourly space velocity of 2, and a hydrogen to hydrocarbon mole ratio of 6. The temperature was adjusted so as to maintain 102 F–1 clear octane product throughout the runs. The results of reforming with the two catalysts can be seen in FIGS. 1 and 2. The graph in FIG. 1 shows that Catalyst C fouls at a much lower rate than Catalyst D. The graph in FIG. 2 shows that significantly higher amounts of 102 F–1 clear octane product are obtained using Catalyst C than are obtained using Catalyst D. In comparison to Catalyst D, Catalyst C showed a significantly better stability, i.e., it was not necessarily to increase the temperature of Catalyst C as rapidly as the temperature of Catalyst D in order to maintain the desired conversion.

A reforming process with a catalyst (Catalyst E) comprising 0.3 weight percent platinum, 0.1 weight percent rhenium, 0.4 weight percent tin, and 1.4 weight percent halogen was carried out under the conditions and using the same feed as in Example 2. The catalyst, prior to use in the process, was activated by calcining it in an air-nitrogen mixture containing about 5 weight percent oxygen at 950° F. The halogen content of the catalyst was raised from a preactivation value of 1.2 weight percent to a post-activation value of 1.4 weight percent by including carbon tetrachloride with the air-nitrogen mixture during the activating. The graphs in FIGS. 3 and 4 indicate that activiated Catalyst E, having a halogen content of 1.4

weight percent, had a very low fouling rate and exhibited very good yield stability when used in a reforming process.

While the invention has been described in connection with specific embodiments thereof, it will be understood the it is capable of further modification and this application is intended to cover any variations, uses, or adaptations of the invention, following, in general, the principles of the invention, and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains, and as may be applied to the essential features hereinbefore set forth, and as fall within the scope of the invention and the limits of the appended claims.

The invention is hereby claimed as follows:

1. A process for reforming a naphtha feedstock, comprising: contacting a naphtha feedstock containing less than about 10 p.p.m. by weight sulfur and less than about 50 p.p.m. by weight water, at reforming conditions and in the presence of hydrogen with a catalytic composition including a porous alumina-containing solid carrier, 0.01 to 3 weight percent platinum, 0.01 to 3 weight percent rhenium, 0.01 to 8 weight percent tin, and 0.1 to 3 weight percent halogen wherein the catalytic composition prior to the contacting is activated by the step comprising reacting the catalytic composition with an activating gas including oxygen and a halogenating component at a temperature from 500 ° F. to 1300° F. for at least about 0.5 hours.

2. A process as in Claim **1** wherein the platinum is from 0.01 to 1.0 weight percent, the rhenium is from 0.01 to 1.0 weight percent, and the tin is from 0.01 to 1.0 weight percent.

3. A process as in Claim **1**, where in the tin is included with the catalytic composition by impregation from an organic solvent.

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HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—140

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,830,727 Dated August 20, 1974

Inventor(s) HARRIS E. KLUKSDAHL and ROBERT G. WALL

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

Col. 1, line 38, "0.01 to 2 weight percent tin" should read --0.01 to 8 weight percent tin--.

Col. 2, line 20, "also yield" should read --also has yield--.

Col. 2, line 39, "0.01 to 8 weight percent tin" should read --0.01 to 3 weight percent tin--.

Col. 3, line 5, "that the" should read --than the--.

Col. 3, lines 9-10, "0.4 weight percent rhenium" should read --0.4 weight percent tin, 0.1 weight percent rhenium--.

Col. 5, line 46, "conent" should read --content--.

Col. 6, line 24, "Hydrodrodesulfurization" should read --Hydrodesulfurization--.

Col. 7, line 9, "perferably" should read --preferably--.

Col. 7, line 28, "activatig" should read --activating--.

Col. 8, line 63, before the paragraph "A reforming process with a catalyst (Catalyst E). . . ." should be the heading --EXAMPLE 3--.

Col. 8, line 75, "activiated" should read --activated--.

Claim 3, line 1, "where in" should read --wherein--.

Signed and sealed this 17th day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents