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PATENT SPECIFICATION

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION

Catalytic reforming process

We, CHEVRON RESEARCH COMPANY, a corporation duly organized under the laws of the State of Delaware, United States of America, and having offices at 200 Bush Street, San Francisco, California, 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:—

This invention relates to hydrocarbon reforming processes, and more particularly to a novel catalytic composition and to a process for reforming of a naphtha fraction in the presence of the novel catalyst. The new catalyst comprises specified proportions of platinum and rhenium supported on a porous solid carrier.

PRIOR ART

Catalytic reforming is well known in the petroleum industry and refers to the treatment of naphtha fractions to improve the octane rating. The more important hydrocarbon reactions occurring during reforming operations employing catalysts comprising dehydrogenation-promoting metal components include dehydrogenation of naphthenes to aromatics, dehydrocyclization of normal paraffins to naphthenes and aromatics, isomerization of normal paraffins to isoparaffins, and hydrocracking of relatively long-chained paraffins. Hydrocracking reactions which produce high yields of light gaseous hydrocarbons, e.g., methane and ethane, are to be particularly avoided during reforming as this decreases the yield of gasoline boiling products. Furthermore, since hydrocracking is an exothermic process, as contrasted to reforming which, in general, is endothermic, hydrocracking reactions which result in the production of high yields of light gaseous products are generally accompanied by severe temperature excursions which can result in temperature runaways in a reforming operation.

Because of the demand for high octane gasoline for use as motor fuels, etc., extensive research is being devoted to the development of improved reforming catalysts and catalytic reforming processes. Catalysts for successful reforming processes must possess good selectivity, i.e., 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 general, high octane number gasoline products can be obtained from a given feed by using more severe conditions of high temperature or low space velocity; however, the gasoline yield generally suffers accordingly as the octane number of the product is increased. Catalysts are thus often rated on the yield-octane number selectivity; i.e., compared on the basis of gasoline yield obtainable at the desired product octane number. The catalysts should also possess good activity in order that the temperature required to produce a certain quality product need not be too high. Apart from good selectivity and activity, it is also necessary that catalysts possess good stability in order that the activity and selectivity characteristics can be retained during prolonged periods of operation.

Catalysts comprising platinum, for example, platinum supported on alumina, are well known and widely used for reforming of naphthas and gasoline boiling range materials in order to produce high octane number gasolines. Platinum catalysts are

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SPECIFICATION AMENDED - SEE ATTACHED SLIP

highly selective toward the production of high octane aromatics and highly active for the several reactions that occur during reforming. However, platinum catalysts are also very expensive because of the high cost of platinum and will probably become even more expensive as a result of the restricted availability of the metal. These economic factors have led the petroleum industry to seek less expensive substitutes for platinum and to investigate catalytic promoters to use with the platinum catalysts to increase their activity, stability, and in particular the gasoline yield-octane number selectivity, thereby making platinum catalysts more economical for reforming operations.

Rhenium has been proposed in the prior art for use in catalytic reforming as a substitute for more common catalytic components such as platinum. However, rhenium has been found to be extremely poor for reforming. Thus, rhenium alone supported on charcoal or alumina was found to possess only limited reforming activity and to require excessively large concentrations of the metal, above 5 weight percent, to obtain good activity. Rhenium has also been suggested for use with palladium for reforming; thus a catalyst comprising palladium and rhenium impregnated on alumina, which catalyst was presulfided, was shown to have better initial reforming activity than a presulfided palladium-alumina catalyst when used to reform a sulfur-containing naphtha. However, the activity of the palladium-rhenium presulfided catalyst decreased significantly after only limited use.

We prepared a catalyst comprising platinum and rhenium composited with alumina, but when tested for the reforming of a naphtha fraction, the catalyst caused excessive hydrocracking. The production of large amounts of light gases, such as methane and ethane, was significantly higher than the production of light gases with a catalyst comprising platinum alone on alumina. In other words, the platinum-rhenium catalytic composition was found to be less selective for the production of high octane gasoline products than a platinum-alumina catalyst. Also, upon introduction of the naptha fraction to the reaction zone, a severe exotherm was observed in the catalyst bed. We also prepared a catalyst comprising platinum and rhenium on alumina, sulfided said catalyst, and tested it for the reforming of a sulfur-containing feed. The catalyst exhibited poor selectivity and activity. The yield of high octane products was low, thus making the reforming process unattractive economically. Thus, although rhenium has been suggested for use for noble metals such as palladium, it was found that such combination was not satisfactory under the above conditions.

It came as a surprising discovery that when certain conditions of operations are followed and/or the catalyst subjected to certain pretreatments, a catalyst comprising platinum and rhenium suported on alumina possesses high activity, and, particularly, good selectivity and stability, for the reforming of sulfur-free feeds. It was especially unexpected to find that a supported platinum-rhenium catalyst would initially show undesirable hydrocracking, and then after reforming is continued the hydrocracking becomes negligible. In fact after the initial period the catalyst comprising platinum and rhenium on alumina is so far superior to a catalyst comprising platinum alone on alumina that the initial poor reforming, which results in the production of high yields of light gaseous hydrocarbons, can be tolerated for the time needed to reduce the excessive hydrocracking activity of the catalyst. It is possible to get longer run lengths with higher yields of high octane products with the platinum-rhenium supported catalyst than with a platinum catalyst without rhenium.

SUMMARY OF THE INVENTION

In accordance with the present invention an improved reforming process can be conducted in the presence of catalysts comprising platinum and rhenium incorporated on or in porous inorganic oxide carriers. Rhenium in small concentrations, less than about 5 weight percent, is effective as a promoter for platinum reforming catalysts, measurably lowering the yield decline rate, i.e., increasing the stability of the catalyst, when sulfur is excluded from the feedstock. Thus, in accordance with the present invention reforming of a substantially sulfur-free naphtha fraction is accomplished by contacting said fraction at reforming conditions and in the presence of hydrogen with a catalyst comprising a porous inorganic oxide catalyst support having disposed thereon in intimate admixture from 0.01 to 3 weight percent of platinum and from 0.01 to 5 weight percent rhenium, based on the total catalyst.

Also, in accordance with the present invention, there is provided a catalyst composition comprising a porous inorganic oxide catalyst support having disposed thereon in intimate admixture from 0.01 to 3 weight percent of platinum and from 0.01 to 5 weight percent rhenium, based on the total catalyst. The novel catalyst of the present invention is found to be highly active and stable for the reforming of naphtha and gasoline boiling-range hydrocarbons, and, in fact, is superior to commercial reforming catalysts containing platinum but no rhenium.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be better understood and will be further explained hereinafter with reference to the graphs in FIGURES 1 and 2 of the accompanying drawings which show, for comparison purposes, data from simulated life tests indicating the reforming activity and stability of a conventional catalyst comprising platinum on an alumina support, and a catalyst comprising platinum and rhenium on an alumina support. The conditions of operation were more severe than normally used in a reforming operation in order to simulate the response of the catalysts to much longer tests (life tests). The graph in FIGURE 1 shows the average catalyst temperatures as a function of length of test or hours on-stream required to maintain a 100-octane (F-1 clear) product for each of the two catalysts. The graph in FIGURE 2 shows as a function of the time on-stream, the yield of C_5+ liquid product, or gasoline having a 100-octane rating produced during reforming with each of the two catalysts. From FIGURE 2 it is seen that the process using the platinum-rhenium catalyst yields significantly higher amounts of 100-octane gasoline product than the process using the platinum catalyst. The catalyst temperatures and C_5+ liquid product volume percents used to make the comparisons in the graphs were obtained only after the hydrocracking activity of the platinum-rhenium catalyst had subsided to that of the platinum catalyst. Thus, the catalysts had been on-stream for several hours before making the comparison shown in the graphs of FIGURES 1 and 2.

THEORY OF THE INVENTION

It is not fully understood why rhenium promotes platinum-containing catalysts for the reforming of naphtha. While not intending to limit the scope of the present invention or be bound by any theoretical explanation, there is evidence indicating that rhenium forms an alloy with the platinum and that this alloy may, in part, be responsible for the improved performance of the platinum-rhenium catalyst over a conventional platinum catalyst.

X-ray and electron diffraction studies of the metallic phases present in catalysts comprising various concentrations of platinum and rhenium supported on alumina indicate platinum-rhenium phase changes remarkably similar to that observed in bulk platnium-rhenium alloy systems, i.e., systems with no support present. Thus, reference to the phase diagram of the bulk platinum-rhenium alloy sister [see, for example, Hansen, M., and Anderko, K., "Constitution of Binary Alloys", McGray Hill (1958)] that for concentrations of rhenium from 0 to about 40 atomic weight percent and at temperatures below at least 1750°C, only one platinum-rhenium phase exists, that of the face center cubic (fcc) crystal structure for platinum. Above 40 atomic percent rhenium, the hexagonal close pack (hcp) structure of rhenium can also be observed. Studies conducted with samples of catalysts comprising platinum alone on alumina, rhenium alone on alumina, and various concentrations of platinum and rhenium on alumina showed that for concentrations of rhenium on the catalyst of less than about 50 atomic weight percent, the hcp rhenium structure was not present, or, at least, could not be detected; only the fcc platinum structure existed. At higher concentrations of rhenium on the catalyst, i.e. above about 50 atomic weight percent rhenium, the hcp rhenium structure could be observed. The platinum-rhenium catalyst samples used to investigate the crystal structure of the metals were prepared by heating the catalysts to elevated temperatures, for example 850°C, in either wet or dry hydrogen to reduce the metals to the metallic state.

It is also known from studies with bulk platinum-rhenium systems that the addition of rhenium to platinum decreases the lattice spacing of the fcc platinum unit cell. The decrease in lattice spacing as rhenium is added to platinum under conditions to form an alloy can be observed from the increase in the angle of diffraction, 2Θ, using CuK_{α_1} radiation, from the (311) plane of the fcc platinum structure. Increasing the rhenium concentration in platinum-alumina catalysts, also produces an increase in the diffraction angle, 2Θ, from the (311) plane of the fcc platinum structure. The addition of rhenium to the platinum-rhenium catalyst causes a large enough shift with the expected direction in magnitude in the diffraction angle, 2Θ, to strongly indicate formation of an alloy.

Additional evidence favoring the theory of alloy formation for platinum-rhenium supported catalysts is the observation that the size of the fcc platinum particles decreases as rhenium is added to platinum-alumina catalysts. The fcc platinum particle size, as determined by electron diffraction investigations of catalyst samples reduced in hydrogen at a constant temperature, decreases as rhenium is added until about the equiatomic platinum-rhenium composition is reached. The metal particle size is related to how easily the metal sinters; i.e., the smaller the particles, the less the metals have sintered. This ease in sintering is in turn related to the melting point of the metals; i.e., the higher the melting point of the metals, the more difficult it is

for sintering to occur. Thus, the decrease in size of the fcc particles as rhenium is added to platinum-alumina catalysts is believed to be due to the increase in melting point of the alloy formed. This observation is consistent with the chemistry of bulk platinum-rhenium alloy systems which show that the addition of rhenium to platinum increases the melting point of the fcc crystals.

DESCRIPTION OF THE INVENTION

The porous solid carrier or support which is employed in the preparation of the platinum-rhenium catalyst of the present invention is an inorganic oxide. A high surface area inorganic oxide carrier is particularly preferred, e.g., an inorganic oxide having a surface area of 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, particularly when acid treated to increase the activity, 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, however, 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.

A particularly preferred catalytic carrier for purposes of this invention is alumina. Any of the forms of alumina suitable as a support 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.

The novel reforming catalysts comprises the desired porous solid catalyst support and disposed thereon in intimate admixture catalytically active amounts of platinum and rhenium. The catalyst proposed for use in the present invention comprises platinum in amounts of from about 0.01 to 3 weight percent and preferably from about 0.2 to 1 weight percent based on the finished catalyst. Concentrations of platinum below about 0.01 weight percent are too low for satisfactory reforming operations, while on the other hand concentrations of platinum above about 3 weight percent are generally unsatisfactory because they produce excessive cracking. Furthermore, due to the high cost of platinum, the amount which can be used is somewhat restricted. The concentration of rhenium in the catalyst composition is from 0.01 to 5 weight percent and preferably 0.1 to 2 weight percent. Higher concentrations of rhenium could be advantageously used but the cost of rhenium limits the amount incorporated on the catalyst. It is preferred that the rhenium to platinum atom ratio be from about 0.2 to about 2.0. More particularly, it is preferred that the atom ratio of rhenium to platinum does not exceed one. Higher ratios (i.e., greater than one) of rhenium to platinum can be used but generally no further significant improvement is obtained.

Although platinum and rhenium can be intimately associated with the porous solid carrier by suitable techniques such as by ion exchange, coprecipitation, etc., the metals are usually associated with the porous solid carrier by impregnation. Furthermore, one of the metals can be associated with the carrier by one procedure, e.g., ion-exchange, and the other metal associated with the carrier by another procedure, e.g., impregnation. As indicated, however, the metals are preferably associated with the carrier by impregnation. The catalyst can be prepared either by coimpregnation of the two metals or by sequential impregnation. In general, the carrier material is impregnated with an aqueous 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 water. Chloroplatinic acid is generally the preferred source of platinum. Other feasible platinum-containing compounds, e.g., ammonium chloroplatinates and polyammineplatinum salts, can also be used. Rhenium compounds suitable for incorporation onto the carrier include, among others, perrhenic acid and ammonium or potassium perrhenates. It is contemplated in the present invention that incorporation of the metals with the carrier can be accomplished at any particular stage of the catalyst preparation. For example, if the metals are to be incorporated onto an alumina support, the incorporation 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 water solution of the metal compounds. Regardless of the method of preparation of the supported platinum-rhenium catalyst it is necessary that the platinum and rhenium be in intimate association with and dispersed throughout the porous solid catalyst support.

Following incorporation of the carrier material with platinum and rhenium, the resulting composite 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 composite can be calcined at an elevated

temperature, e.g., up to about 1200°F, if desired.

The carrier containing platinum and rhenium is preferably heated at an elevated temperature to convert the platinum and rhenium to the metallic state. Preferably the heating is performed in the presence of hydrogen, and more preferably, dry hydrogen. In particular, it is preferred that this prereduction be accomplished at a temperature in the range of 600°F to 1300°F, and preferably 600°F to 1000°F.

Reforming with certain of the catalysts of the present invention initially produces an excessive amount of light hydrocarbon gases unless proper pretreatment or startup techniques are utilized. The light hydrocarbon gases are produced as a result of the high hydrocracking activity or metal-cracking activity of the catalyst. It has been found that the hydrocracking activity can be diminished if the catalyst is sulfided prior to contact with naphtha. The presulfiding can be done in situ or ex situ by passing a sulfur-containing gas, for example, H_2S, through the catalyst bed. 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 effectively reduces the initial hydrocracking activity of the catalyst. The exact form of sulfur used in the sulfiding process is not critical. The sulfur can be introduced into the reaction zone in any convenient manner and at any convenient location. It can be contained in the liquid hydrocarbon feed, the hydrogen-rich gas, the recycle liquid stream or a recycle gas stream or any combination. After operating the reforming process in the presence of sulfur for a period of time short in comparison with the over-all run length that can be obtained with the novel catalyst, the addition of sulfur must be discontinued in order to realize the full benefits of the present invention such as decreased yield decline rate or improved stability. The period of time required to reduce the initial hydrocracking activity will vary from several hours to several hundred hours depending on the amount of sulfur used, the severity of operation, and the platinum/rhenium ratio. The time required to reduce the initial hydrocracking activity will vary inversely to the amount of sulfur, the severity and the platinum/rhenium ratio.

It has also been found that a small amount of an oxyanion of sulfur, such as a sulfate, sulfite, bisulfate, or bisulfite, associated with the catalyst composition imparts beneficial properties to the catalyst, e.g., helps to control the initially high hydrocracking activity. Thus, for example, sulfate associated with a catalyst comprising alumina and catalytically active amounts of platinum and rhenium reduces the yield of light hydrocarbon gases initially produced during reforming as well as during the dehydrocyclization of normal heptane to aromatics. The oxyanions of sulfur can be incorporated onto the catalyst composition during preparation of the porous solid carrier. For example, in the preparation of an alumina carrier, the aluminum salt used as a starting material can be the sulfate form. Precipitation of alumina generally results in a minor amount of sulfate associated with the alumina. An oxyanion of sulfur can also be incorporated onto the catalyst carrier by contacting the previously prepared carrier with suitable compounds containing oxyanions of sulfur, e.g., $SO_4^=$, $SO_3^=$, HSO_4^-, or HSO_3^-. The oxyanions of sulfur for purposes of the present invention can advantageously be present in the final catalyst in an amount from 0.05 to 2 weight percent and preferably from 0.1 to 1 weight percent.

The catalyst of the present invention preferably exists during the reforming process with the platinum and rhenium in the metallic state. Thus, even though the catalyst is contacted with sulfur, and the metals apparently converted to the sulfide form, prior to or during reforming in order to reduce the initial hydrocracking activity of the catalyst, the catalyst is stripped of sulfur during the initial period of reforming. Thus, the sulfur will have been stripped off, and the metals, platinum and rhenium, converted to the metallic state, in approximately the same length of time necessary to reduce the high hydrocracking activity. In order for the metals to exist in a sulfided form throughout the reforming process, sulfur would have to be continually added to the catalyst. But, sulfur addition throughout the reforming process is not satisfactory for the purposes of the present invention.

The catalyst can be promoted for reforming by the addition of halides, particularly fluoride or chloride. The halides apparently provide a limited amount of acidity to the catalyst which is beneficial to most reforming operations. A catalyst promoted with halide preferably contains from 0.1 to 3 weight percent total halide content. The halides can be incorporated onto the catalyst carrier at any suitable stage of catalyst manufacture, e.g. prior to or following incorporation of the platinum and rhenium. Some halide is often incorporated onto the carrier when impregnating with the platinum; for example, impregnation with chloroplatinic acid normally results in chloride addition to the carrier. Additional halide may be incorporated onto the support simultaneously with incorporation of the metal if so desired. In general, the halides are combined 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 fluoride or chloride is incorporated onto the carrier from an aqueous solution containing the halide.

Generally the form in which the catalyst is prepared is controlled by the manipulative process to which it will be subjected. Thus, if the reforming process of the present invention is to be conducted in a fixed bed or moving bed process, the catalyst mixture will be formed into tablets, pellets, spheroidal particles, or extruded particles; whereas if a fluidized bed operation is desired, the catalyst will be provided in a finely-divided form.

The feedstock to be employed in the reforming operation is a light hydrocarbon oil, for example, a naphtha fraction. Generally, the naphtha will boil in the range falling within the limits of from about 70° to 550°F and preferably from 150° to 450°F. The feedstock can be, for example, either a straight-run naphtha or a thermally cracked or catalytically cracked naphtha or blends thereof. The feed should be essentially sulfur free; that is, the feed should preferably contain less than about 10 ppm sulfur and more preferably less than 5 ppm, and still more preferably less than 1 ppm. The presence of sulfur in the feed decreases the activity of the catalyst as well as its stability.

In the case of a feedstock which is not already low in sulfur, acceptable 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 and a minor proportion of molybdenum oxide and cobalt oxide. Hydrodesulfurization is ordinarily conducted at 700-850°F, at 200 to 2000 psig, and at a liquid hourly space velocity of 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.

The reforming conditions 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 within the range of about 600° to 1100°F and preferably about 700° to 1050°F. The pressure in the reforming reaction zone can be atmospheric, or superatmospheric; however, the pressure will in general lie within the range from about 25 to 1000 psig and preferably from about 50 to 750 psig. 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 10 and preferably from 1 to 5.

Reforming generally results in the production of hydrogen. 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 introduced 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. Hydrogen is preferably introduced into the reforming reactor at a rate varying from about 0.5 to about 20 moles of hydrogen per mole of feed. The hydrogen can be in admixture with light gaseous hydrocarbons. Excess hydrogen removed after separation from the products will generally be purified and recycled to the reaction zone.

After a period of operation when the catalyst becomes deactivated by the presence of carbonaceous deposits, the catalyst can be reactivated or regenerated by passing an oxygen-containing gas, such as air, into contact with the catalyst 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 are well known in the art.

The process of the present invention will be more readily understood by reference to the following examples.

Example 1

A conventional, rhenium-free catalyst comprising 0.7 weight percent platinum on alumina was tested and compared for cyclohexane dehydrogenation activity with a series of catalysts comprising various rhenium levels on the aforementioned platinum-alumina composition.

The platinum-alumina catalyst was prepared by impregnating alumina with chloroplatinic acid. The platinum-rhenium-alumina catalysts were prepared by impregnating previously impregnated platinum-alumina catalysts with aqueous solutions

containing perrhenic acid in sufficient concentrations to provide the desired level of rhenium on the finished catalysts. Drying was accomplished by heating the catalysts for 12 hours at 170°F and then for 3 hours at 400°F. The catalysts impregnated with platinum or platinum and rhenium were subjected to a hydrogen atmosphere at a rate of 6.9 liters H_2 per minute per gram of catalyst for two hours at various temperatures.

The cyclohexane dehydrogenation runs were conducted at a temperature of 485°F, a pressure of one atmosphere, and a hydrogen to hydrocarbon (cyclohexane) ratio of 10. The hydrogen rate to the reactor was 6.9 liters H_2 per minute per gram catalyst. Cyclohexane was contacted with the catalyst at a rate of 0.17 liters liquid hydrocarbon per hour per gram of catalyst. Cyclohexane dehydrogenation rates, measured in terms of micromoles benzene produced per gram of catalyst per hour, were determined for the different catalysts having different rhenium contents and prereduced at different temperatures. The results are presented in Table I.

TABLE I

Cyclohexane Dehydrogenation Rates

Hydrogen Prereduction	*Wt. % Re on Alumina Carrier Containing 0.7 Wt. % of Platinum*				
Temp. °F	*0*	*0.2*	*0.4*	*0.7*	*1.4*
800	39	—	—	—	54
1000	37	48	50	54	58
1200	—	55	—	46	—
1400	35	47	—	47	64
1600	15	35	—	37	55

The catalysts containing platinum and rhenium were in all instances more active for the dehydrogenation of cyclohexane than the catalyst containing only platinum. Thus, for example, the catalyst containing 0.7 weight percent rhenium and 0.7 weight percent platinum and prereduced at 1000°F had a cyclohexane dehydrogenation rate of 54 as compared to the cyclohexane dehydrogenation rate of 37 for the platinum catalyst prereduced at 1000°F and containing no rhenium. Furthermore, it is noted that the dehydrogenation rate for the catalyst containing only platinum falls off more rapidly with increasing prereduction temperature than the catalysts containing rhenium in addition to platinum. For example, the catalyst containing only platinum and prereduced at 1000°F had a dehydrogenation rate of 37 whereas the same catalyst prereduced at a temperature of 1600°F had a dehydrogenation rate of only 15, a decrease of more than half. The catalyst containing 0.2 weight percent rhenium in addition to platinum, and prereduced at 1000°F, however, had a dehydrogenation rate of 48 compared to a dehydrogenation rate of 35 for the same catalyst prereduced at a temperature of 1600°F. This is a decrease of less than one-third, and indicates that the platinum-rhenium catalysts are more stable than platinum catalysts containing no rhenium.

Example 2

A catalyst containing 0.7 weight percent platinum and 0.7 weight percent rhenium on an alumina carrier was compared with a catalyst containing 0.7 weight percent platinum in an accelerated reforming process. Catalysts were prepared and dried as described in Example 1, and then heated in hydrogen for about ½ hour at 450°F and about 1½ hours at 700°F. The hydrogen flow rate in all instances was 4.0 milliliters H_2 per minute per gram catalyst.

The feed used in the reforming operation was a hydrofined, catalytically cracked naphtha having an initial boiling point of 151°F, an end point of 428°F and a 50 percent boiling point of 307°F. The research octane number of the feed without antiknock additives (F-1 clear) was 64.6. The naphtha contained less than 0.1 ppm nitrogen or sulfur. The reaction zone conditions were maintained at a pressure of 300 psig, a liquid hourly space velocity of 3, and a temperature sufficient to produce a C_5+ product with an octane rating (F-1 clear) of 100. Thus, the temperature in the reaction zone, as measured by the average catalyst bed temperature, was changed with time in order to maintain a product having 100 octane. The reforming process was conducted under conditions to simulate a life test for the catalyst. That is, conditions were not necessarily maintained at levels used in a commercial reforming process but were, in general, more severe in order to test, in a relatively short time of a few hundred hours, how well the catalyst would perform in a commercial operation. Hydrogen produced during the reforming process was circulated to the reaction zone to provide about 5.3 moles hydrogen per mole hydrocarbon feed.

The above comparison of Example 2 between the catalyst containing platinum and rhenium and the catalyst containing only platinum is shown in the appended figures. The change in average catalyst temperature needed in order to maintain the desired 100-octane (F-1 clear) product is shown in FIGURE 1, and the yield of C_5+ gasoline having an octane rating of 100 is shown in FIGURE 2. The response of the platinum

catalyst to the simulated life test was very poor. As seen in FIGURE 1 it was necessary to increase the temperature exorbitantly in order to maintain a 100-octane (F-1 clear) product. Moreover, the yield of C_5+ liquid product having the desired octane rating decreased significantly with time as shown in FIGURE 2. On the other hand, the catalyst containing platinum and rhenium displayed remarkable activity during the accelerated reforming test. From FIGURE 2 it can be seen that the naphtha feed was reformed to yield nearly 86 volume percent C_5+ product, having a 100-octane (F-1 clear) rating, over almost the entire period of time of the test. From FIGURE 1 it can be seen that the reforming temperature required to maintain a 100 octane (F-1 clear) product increased only slightly as compared to the temperature increase in reforming with the platinum catalyst. It is apparent that rhenium improves the stability and activity of the platinum catalyst for reforming.

In Example 2, reforming with the catalyst comprising platinum and rhenium initially produced high yields of light hydrocarbon gases, particularly methane and ethane, compared to reforming with the catalyst comprising platinum without rhenium. Approximately 170 hours of reforming were necessary in order to bring the light gas production with the platinum-rhenium catalyst down to the level of light gas production of the platinum catalyst. A large exotherm was also observed during the initial period of reforming with the platinum-rhenium catalyst. As an indication of the high yield of light gases produced during this initial break-in period, measurements after 43 hours of operation showed 25.7 weight percent of the feed being converted to light hydrocarbon gases. The data used to make the comparison shown in the graphs in FIGURES 1 and 2 were obtained only after the yield of light gases using the platinum-rhenium catalyst approximated that of the platinum catalyst, i.e., after the initial 170 hours of operation.

The following examples illustrate the detrimental effect of sulfur in the feed on to the catalytic reforming process of the present invention.

Example 3

Two samples of catalyst were prepared and dried, as in Example 1, comprising 0.7 weight percent platinum and 0.7 weight percent rhenium supported on an alumina carrier. The samples were prereduced under various conditions and tested for the dehydrocyclization of n-heptane to aromatics. One sample, referred to as catalyst A, was contacted with hydrogen for 2 hours at 1000°F and atmospheric pressure, and then for 2 hours at 900°F and 250 psig. The other sample, referred to as catalyst B, was contacted with hydrogen for 2 hours at 1000°F and 250 psig. The hydrogen flow rate was 1.4 milliliters gas per minute per gram of catalyst. The two catalyst samples were tested for the dehydrocyclization of n-heptane under reaction conditions including a temperature of 900°F and a pressure of 250 psig. Hydrogen was added to the reaction zone at a mole ratio of hydrogen to n-heptane of 6. The n-heptane feed was contacted with the catalysts at a rate of about 80 milliliters n-heptane per hour per gram of catalyst. The n-heptane feed was sulfur-free when used with catalyst A; however, sulfur (200 ppm) was present in the feed used with catalyst B. The results of the dehydrocyclization runs are presented in Table II.

TABLE II

	Catalyst A	B
Sulfur in Feed, ppm	0	200
Moles Aromatic Produced/ 100 Moles Feed	8.3	0.9

As can be seen from the above data, subjecting the catalyst containing platinum and rhenium to sulfur, has a deleterious effect upon the catalyst selectivity.

Example 4

A catalyst comprising approximately 0.6 weight percent platinum and 0.46 weight percent rhenium was prepared by impregnating a previously impregnated platinum-alumina support with an aqueous solution containing perrhenic acid. The catalyst was dried overnight in nitrogen at 300°F and then heated for 200 hours in air at 700°F and 400 hours in air at 900°F. Thereafter the catalyst comprising alumina impregnated with platinum and rhenium was subjected for one-half hour to a hydrogen atmosphere at 700°F to reduce the metals. The catalyst was used in a reforming process using the feed described in Example 2. Different levels of sulfur were introduced into the feed during the process. The reforming conditions included a pressure of 500 psig, an LHSV of 2, and a hydrogen to hydrocarbon mole ratio of about 8.

The feed initially contained less than 0.1 ppm sulfur. The F-1 clear octane rating of the product produced during reforming was 97 with the average catalyst temperature being 920°F. 50 ppm sulfur was introduced into the feed. The product octane number dropped to 91 and the average catalyst temperature increased to 929°F. On the addition of 500 ppm sulfur to the feed, the product octane number dropped to 86 and the average catalyst temperature increased to

935°F. The C_5+ liquid volume yield remained approximately the same in all instances, i.e. at about 84 to 85 volume percent. The results are tabulated in Table III.

TABLE III

Sulfur In Feed, ppm	*Average Catalyst Temperature, °F*	*Product F-1 Clear Octane Number*
0	920	97
50	929	91
500	935	86

The detrimental effect of the presence of sulfur in the feed is readily apparent. The presence of sulfur in the feed decreases the endothermic reforming reactions which produce high octane gasoline. Thus, the catalyst temperature increases and the octane number decreases.

Example 5

A catalyst comprising 0.66 weight percent platinum and 0.22 weight percent rhenium was prepared by coimpregnating an alumina support with platinum as chloroplatinic acid and rhenium as perrhenic acid. The catalyst was dried and then reduced in hydrogen.

The catalyst was used to reform the hydrofined catalytically cracked naphtha described in Example 2. The reaction conditions included a pressure of 500 psig, an LHSV of 3, and a hydrogen to hydrocarbon mole ratio of 5.3. The temperature was controlled throughout the reforming process to produce a 100 F-1 clear octane number product. The feed initially contained less than 0.1 ppm sulfur. The starting temperature of the reforming process was about 940°F. During the first 845 hours of operation, the catalyst exhibited a low fouling rate; for example, from about 200 hours to 845 hours, the fouling rate was about 0.024°F per hour. After approximately 845 hours of operation, 10 ppm sulfur were added to the feed. The temperature required to make 100 F-1 clear octane gasoline increased 20 degrees, that is, the catalyst became 20 degrees less active as a result of sulfur addition. After the removal of sulfur, the catalyst regained a small amount of activity but did not return to the activity which it exhibited prior to the addition of sulfur to the feed. The fouling rate of the catalyst after having seen sulfur was 0.045°F per hour. Thus, it can be seen that even a small amount of sulfur in the feed, for example, 10 ppm, has detrimental effects on the catalyst.

WHAT WE CLAIM IS:—

1. Process for reforming a substantially sulfur-free naphtha fraction, which comprises subjecting the fraction to contact at reforming conditions and in the presence of hydrogen with a catalyst comprising a porous inorganic oxide catalyst support having disposed thereon in intimate admixture from 0.01 to 3 weight percent of platinum and from 0.01 to 5 weight percent of rhenium, based on the total catalyst.

2. Process according to claim 1, wherein said catalyst contains from 0.2 to 1 weight percent of platinum and from 0.1 to 2 weight percent of rhenium.

3. Process according to claim 1 or 2, wherein the porous inorganic oxide is one having a surface area of 50-700 m^2/gm.

4. Process according to claim 1, 2 or 3, wherein said support is alumina.

5. Process according to any preceding claim, wherein said catalyst contains as a promoter a total of from 0.1 to 3 weight percent of halide selected from chloride and fluoride.

6. Process according to any preceding claim, wherein said catalyst initially contains from 0.05 to 2 weight percent of an oxyanion of sulfur.

7. Process according to any preceding claim, wherein sulfur is excluded from the naphtha fraction feed throughout the period of contact of said catalyst with the feed, except during the period when feed is first contacted with said catalyst which is substantially free of sulfur.

8. Process in accordance with claim 1 for reforming a substantially sulfur-free naphtha fraction, substantially as described in any one of the foregoing Examples.

9. A catalyst composition comprising a porous inorganic oxide catalyst support having disposed thereon in intimate admixture from 0.01 to 3 weight percent of platinum and from 0.01 to 5 weight percent of rhenium, based on the total catalyst.

10. A composition as claimed in claim 9, wherein the catalyst contains from 0.2 to 1 weight percent of platinum and from 0.1 to 2 weight percent of rhenium.

11. A composition as claimed in claim 9 or 10, wherein the porous inorganic oxide is one having a surface area of 50-700 m^2/gm.

12. A composition as claimed in Claim 9, 10 or 11, wherein said support is alumina.

13. A composition as claimed in claim 9, 10, 11 or 12, wherein the catalytic composition contains from 0.05 to 2 weight percent of an oxyanion of sulfur.

935°F. The C_5+ liquid volume yield remained approximately the same in all instances, i.e. at about 84 to 85 volume percent. The results are tabulated in Table III.

TABLE III

Sulfur In Feed, ppm	*Average Catalyst Temperature, °F*	*Product F-1 Clear Octane Number*
0	920	97
50	929	91
500	935	86

The detrimental effect of the presence of sulfur in the feed is readily apparent. The presence of sulfur in the feed decreases the endothermic reforming reactions which produce high octane gasoline. Thus, the catalyst temperature increases and the octane number decreases.

Example 5

A catalyst comprising 0.66 weight percent platinum and 0.22 weight percent rhenium was prepared by coimpregnating an alumina support with platinum as chloroplatinic acid and rhenium as perrhenic acid. The catalyst was dried and then reduced in hydrogen.

The catalyst was used to reform the hydrofined catalytically cracked naphtha described in Example 2. The reaction conditions included a pressure of 500 psig, an LHSV of 3, and a hydrogen to hydrocarbon mole ratio of 5.3. The temperature was controlled throughout the reforming process to produce a 100 F-1 clear octane number product. The feed initially contained less than 0.1 ppm sulfur. The starting temperature of the reforming process was about 940°F. During the first 845 hours of operation, the catalyst exhibited a low fouling rate; for example, from about 200 hours to 845 hours, the fouling rate was about 0.024°F per hour. After approximately 845 hours of operation, 10 ppm sulfur were added to the feed. The temperature required to make 100 F-1 clear octane gasoline increased 20 degrees, that is, the catalyst became 20 degrees less active as a result of sulfur addition. After the removal of sulfur, the catalyst regained a small amount of activity but did not return to the activity which it exhibited prior to the addition of sulfur to the feed. The fouling rate of the catalyst after having seen sulfur was 0.045°F per hour. Thus, it can be seen that even a small amount of sulfur in the feed, for example, 10 ppm, has detrimental effects on the catalyst.

WHAT WE CLAIM IS:—

1. Process for reforming a substantially sulfur-free naphtha fraction, which comprises subjecting the fraction to contact at reforming conditions and in the presence of hydrogen with a catalyst comprising a porous inorganic oxide catalyst support having disposed thereon in intimate admixture from 0.01 to 3 weight percent of platinum and from 0.01 to 5 weight percent of rhenium, based on the total catalyst.

2. Process according to claim 1, wherein said catalyst contains from 0.2 to 1 weight percent of platinum and from 0.1 to 2 weight percent of rhenium.

3. Process according to claim 1 or 2, wherein the porous inorganic oxide is one having a surface area of 50-700 m^2/gm.

4. Process according to claim 1, 2 or 3, wherein said support is alumina.

5. Process according to any preceding claim, wherein said catalyst contains as a promoter a total of from 0.1 to 3 weight percent of halide selected from chloride and fluoride.

6. Process according to any preceding claim, wherein said catalyst initially contains from 0.05 to 2 weight percent of an oxyanion of sulfur.

7. Process according to any preceding claim, wherein sulfur is excluded from the naphtha fraction feed throughout the period of contact of said catalyst with the feed, except during the period when feed is first contacted with said catalyst which is substantially free of sulfur.

8. Process in accordance with claim 1 for reforming a substantially sulfur-free naphtha fraction, substantially as described in any one of the foregoing Examples.

9. A catalyst composition comprising a porous inorganic oxide catalyst support having disposed thereon in intimate admixture from 0.01 to 3 weight percent of platinum and from 0.01 to 5 weight percent of rhenium, based on the total catalyst.

10. A composition as claimed in claim 9, wherein the catalyst contains from 0.2 to 1 weight percent of platinum and from 0.1 to 2 weight percent of rhenium.

11. A composition as claimed in claim 9 or 10, wherein the porous inorganic oxide is one having a surface area of 50-700 m^2/gm.

12. A composition as claimed in Claim 9, 10 or 11, wherein said support is alumina.

13. A composition as claimed in claim 9, 10, 11 or 12, wherein the catalytic composition contains from 0.05 to 2 weight percent of an oxyanion of sulfur.

14. A catalyst composition in accordance with claim 9, substantially as described in any one of the foregoing Examples 1 to 3.

15. A catalyst composition in accordance with claim 9, substantially as described in the foregoing Example 4 or 5.

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SPECIFICATION NO 1151639

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated 3 August 1972 this Specification has been amended under Section 14 in the following manner:-

Page 1, line 14, *delete* a novel catalytic composition and to

Page 1, lines 16 and 17, *delete* the novel catalyst. The new catalyst comprises *insert* a catalyst comprising

Page 2, *delete* lines 68 to 70 *insert* after exhibiting high initial hydrocracking activity under usual reforming operating conditions, a catalyst comprising

Page 2, lines 108 and 109, page 9, lines 67 and 68 *delete* substantially sulfur free naphtha fraction *insert* naptha fraction containing less than 10 ppm of sulfur

Page 2, line 116, page 9, line 76, *after* catalyst *insert* , the contacting being continued at least for a time sufficient to enable the catalyst to exhibit a fouling rate and yield decline which are lower than those which would be exhibited under the same conditions by a catalyst which is identical save that it contains no rhenium

Page 2, *delete* lines 117 to 124 *insert* The catalyst used in the

Page 4, line 46, *delete* novel

Page 5, line 13, *delete* of *insert* used in

Page 5, line 15, *after* gases *insert* when operating under usual reforming conditions,

Page 5, line 88, *delete* of *insert* employed in

Page 6, line 31, *delete* preferably

Page 6, line 32, *delete* more

Page 6, line 33, *delete* still

Page 9, *delete* lines 106 to 125

Page 10, *delete* lines 1 to 6

THE PATENT OFFICE
1 November 1974

R 78220/8

ERRATUM

Slip No 2

SPECIFICATION NO 1151639

Page 4, line 46, *for* catalysts *read* catalyst

THE PATENT OFFICE
26 November 1974

R 78384/1