This invention relates to a catalytic composite especially useful in reforming petroleum hydrocarbons. More particularly, the present invention is directed to an improved catalytic reforming process for obtaining gasoline of high octane number carried out in the presence of a catalyst consisting essentially of a co-gelled chromia-alumina composite of particularly defined composition combined in a particular manner with a specified minor proportion of boria and to the resultant catalytic composite.

Reforming operations wherein hydrocarbon fractions such as naphtha, gasolines and kerosene are treated to improve the anti-knock characteristics thereof, are well known in the petroleum industry. Reforming is generally carried out by contacting the hydrocarbon charge at an elevated temperature in the presence of hydrogen with a suitable catalyst. The temperature generally employed in reforming is between about 700° F. and about 1000° F. and more usually between about 800° F. and about 975° F. The pressure during reforming is generally within the range of about 100 to about 1000 p.s.i.g. and preferably between about 200 and about 700 p.s.i.g. The liquid hourly space velocity employed, i.e., the liquid volume of hydrocarbon per hour per volume of catalyst, is generally between about 0.1 and about 10 and preferably between about 0.5 and about 4. In general, the molar ratio of hydrogen to hydrocarbon charge stock employed is between about 1 and about 20 and preferably between about 4 and about 12.

Hydrocarbon charge stocks generally subjected to reforming comprise mixtures of hydrocarbons and particularly petroleum distillates boiling within the approximate range of 60° F. to 425° F. which range includes gasolines, naphthas, and kerosene. The gasoline fraction may be a full boiling range gasoline or a selected fraction such as naphtha having an initial boiling point of between about 150° F. and about 250° F. and an end boiling point of between about 350° F. and about 425° F. Straight run gasolines generally contain naphthenic hydrocarbons, particularly cyclohexane and related compounds and paraffinic hydrocarbons which are usually of straight chain or slightly branched chain structure, as well as varying proportions of aromatic hydrocarbons. During reforming, a multitude of reactions take place, including isomerization, dehydrogenation, cyclization, etc., to yield a product of increased aromatic content. Thus, in reforming, it is desired to dehydrogenate the naphthenic hydrocarbons to produce aromatics, to cyclize the straight chain paraffinic hydrocarbons to form aromatics, and to effect a controlled type of cracking which is selective both in quality and quantity.

Controlled or selective cracking is highly desirable during reforming since such will result in a product of anti-knock characteristics. As a general rule, the lower molecular weight hydrocarbons exhibit a higher octane number, and a gasoline product of lower average molecular weight will usually have a higher octane number. In addition, the isomerization and molecular rearrangement which occur during reforming to improve the product having higher anti-knock characteristics. The splitting or cracking of carbon to carbon linkages must, however, be selective and should be such as not to result in substantial decomposition of normally liquid hydrocarbon into normally gaseous hydrocarbons. The selective cracking desired ordinarily involves removal of one or two lower alkyl groups, such as methyl or ethyl, from a given molecule in the form of methane or ethane. Thus, during reforming, it is contemplated that heptane may be converted to hexane, nonane to octane or heptane, etc. Uncontrolled cracking, on the other hand, would result in decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons. For example, non-selective cracking of normal octane would ultimately lead to eight molecules of methane.

Uncontrolled reforming, moreover, generally results in rapid formation and deposition on the catalyst of large quantities of a carbonaceous material generally referred to as "coke." The deposition of coke on the catalyst surface diminishes or destroys its catalyzing effect and results in shorter processing periods with the accompanying necessity of frequent regeneration by burning the coke therefrom. In those instances where the activity of the catalyst is destroyed, it is necessary to shut down the unit, remove the deactivated catalyst, and replace it with new catalyst. Such practice obviously is time-consuming and inefficient, imparting a greater over-all expense to the reforming operation.

The choice of catalyst for promoting reforming of hydrocarbons to gasolines of enhanced octane rating is dependent on several factors. Such catalyst should desirably be capable of effecting reforming in a controlled manner as discussed above to yield a product of improved anti-knock characteristics. The catalyst selected should be further be resistant to poisoning and particularly to sulfur poisoning so that sulfur-containing stocks may undergo reforming without the necessity of subjecting the same to a preliminary treatment for desulfurization. The catalyst also should desirably be characterized by high stability and be capable of easy regeneration, and the method for preparing such catalyst should be commercially attractive, requiring a minimum of equipment and processing stages.

In accordance with the present invention, a catalyst of the above-defined characteristics has been discovered.

Broadly, the present invention comprises reforming hydrocarbon mixtures and, particularly a naphthenic fraction of petroleum in the presence of a catalyst consisting essentially of co-gelled chromia and alumina combined with a minor proportion of boria. The invention further comprises the resulting catalyst consisting of a major proportion of alumina, a minor proportion of chromium and a minor proportion of boria combined in a particular manner under conditions such that a completely homogeneous active surface is obtained.

It has herefore been known to employ composites of oxides of chromium and aluminum as catalysts for various reactions. Chromia-alumina composites heretofore recommended as reforming catalysts have been found to be characterized by a certain amount of intraparticle material indicated by the amount of Cr₂O₃ and of the crystalline form during use. Catalysts of the present invention consisting essentially of co-gelled chromia-alumina...
3

composted with boria have unexpectedly, been found to have improved reforming activity in comparison with chromia-alumina composites.

The method of reforming petroleum hydrocarbons in the presence of a co- bloggers chromia-alumina composite combined with boria as described herein has been found to have certain advantages over the processes commercially available. The advantages obtained upon reforming with the present catalyst, while not fully understood, are believed to result from the method of preparation of the catalyst employed. The present catalyst initially involves the formation of a hydrogel of chromia and alumina preferably containing a chromia-alumina content of at least 10 percent by weight and thereafter combining the washed hydrogel with boria.

Boria may be combined with the co- bloggers chromia-alumina by impregnating either the washed hydrogel or the dried and tempered chromia-alumina composite with a solution of a boron compound, followed by drying and calcining of the impregnated product. A preferred embodiment of the invention is the catalytic composite resulting from intimate admixing, for example, by ball-milling chromia-alumina hydrogel and a compound of boria, preferably decomposable boron oxide, sufficiently until a homogeneous composite is obtained and subsequently drying and calcining at an elevated temperature sufficient to effect decomposition of the compound of boron employed to boron oxide but not exceeding about 1000 °F. In one embodiment chromia-alumina hydrogel containing, on a dry basis, about 15 to about 45 percent by weight of chromia and about 55 to about 85 percent by weight of alumina and having a solids content of at least about 10 percent by weight and generally in the approximate range of 10 to 30 percent by weight, i.e., containing about 70 to about 90 percent by weight of water, is ball milled with a finely divided solid boron compound, thermally decomposable to boron oxide, and subsequently dried and calcined at an elevated temperature. The amount of boron compound used may be varied depending on the catalyst composition desired and on the particular compound of boron employed. Boric acid is particularly preferred as a source of the boria component. After intimately admixing by ball milling or other suitable means, the resulting composite is dried and calcined at a temperature sufficient to effect decomposition of the boron compound employed but not in excess of about 1000 °F. The composite catalyst consisting essentially of a co- bloggers alumina and chromia combined with boria is thereafter ready for use.

Composites consisting of a mixture of alumina, a minor proportion of chromia and a minor proportion of boria are suitably prepared in accordance with the above method. Catalysts having a composition of 10 to 30 percent by weight of chromia, 50 to 89 percent by weight of alumina and 1 to 20 percent by weight of boria are unusually effective for promoting reforming operations in which a saturated gasoline is subjected to conversion to produce a reformed gasoline of improved anti-knock properties. Catalysts having a boria concentration in the range of 3 to 10 percent are particularly preferred, whether the present invention to 2. Thus, the cobalt compound, in the form of a catalyst, represents a preferred embodiment of the invention and has been found to afford an improved yield of reformate of the same octane number as compared to an operation carried out under identical reforming conditions employing a chromia-alumina gel catalyst of comparable composition but which had not been composited with boria.

The method of the invention provides a simple but highly effective procedure for preparation of boria containing reforming catalyst. The co- bloggers chromia-alumina is a true gel prepared by forming a hydrogel of chromia and alumina and permitting said hydrogel to set to an all-embracing hydrogel. The hydrogel is suitably in particle form prior to admixture with the boron compound. The particles may be of irregular size such as by breaking up a previously set hydrogel or the particles may be of a uniform size and shape. Preferably, the alumina-chromia hydrogel particles are in the form of spheres prepared by introducing the hydrogel in the form of globules into a water-immiscible medium wherein the hydrogel globules set to spherical hydrogel particles. It is particularly preferred to prepare a co- bloggers catalytic composite of chromia and alumina from a hydrogel having an inorganic oxide content of at least about 10 percent by weight in accordance with the process described in U.S. Patent No. 2,773,839 to Stover and Wilson. Such process has been set forth in detail in the aforementioned patent. For convenience herein, the following is offered as a brief description of said process.

A true, all-embracing chromia-alumina hydrogel having a metal oxide product concentration of at least about 10 percent by weight of alumina in the product, i.e., less than 2 hours and preferably less than 60 seconds, is prepared by intimately admixing an organic chromia salt, such as chromic acid, and an alkali metal aluminate, such as sodium aluminate, to produce a chromia-alumina hydrogel. The hydrogel so formed is permitted to set to a hydrogel. The resulting hydrogel is thereafter subjected to aging and then water-washed. The relative proportions of chromia and alumina may be varied over a wide range. In accordance with the instant invention, however, the concentrations of reactants employed should be such as to afford a chromia-alumina hydrogel of composition within the range set forth hereinafter.

It is preferred, in preparing the above-described hydrogels, to use aqueous solutions of sodium aluminate and chromic acid. Neither of these substances is a true chemical compound. The ratio of sodium to aluminum can be varied widely as can the ratio of acetate to chromium ion. Variation in the sodium to aluminum ratio of the aluminate solution requires compensating adjustment of the acetate to chromium ratio of the chromic acetate solution in order to achieve satisfactory gelation. Hydrosols capable of setting to hydrogels in less than about 20 seconds are particularly desirable for the production of bead-like spherical particles by methods well known in the art, for example, those described in patents to Marion, supra and to Marion and Petrovitch, supra.

Quick-setting hydrosols of low viscosity which can be readily handled at bead-forming nozzles are those prepared from sodium aluminate solutions which have a sodium to aluminum mole ratio referred to as "R" of between 1 and 1.5. The acetate to chromium mole ratio in the chromic acetate solution employed should be not less than 2.8R-1.8 and not more than 4R-2.3 and preferably in the range of 4R-2.8 to 4R-2.4.

The control of the mole ratios discussed above is readily achieved in the manufacture of reactant solutions. Chromium acetate is readily formed by the introduction of undesirable extraneous materials by reducing sodium dichromate with glycine acid in the presence of acetic acid as described more fully in U.S. 2,615,031.

Sodium aluminate is conveniently prepared from casings and other solid boron compounds, i.e., borax or boron acid, represents a preferred embodiment of the invention and has been found to afford an improved yield of reformate of the same octane number as compared to an operation carried out under identical reforming conditions employing a chromia-alumina gel catalyst of comparable composition but which had not been composited with boria.

The sodium to aluminum mole ratio in the range of 1.25/1 to 1.5/1, the sodium aluminate is advantageously manufactured in an open agitated kettle at 220-230 °F. with a reaction time of 1 to 3 hours. Solutions having a lower mole ratio down to about 1.0/1 are made in an autoclave at 240-300 °F. and 10 to 15 pounds per square inch gauge at the same reaction time. Sodium aluminate solutions having a low sodium to aluminum ratio less than 1.3 are relatively unstable and may be stabilized.
by the addition of such organic materials as glycerine, starch, sugar, and the like.

Thus, chromia-alumina hydrogels having a short time of set and a high solids content generally between about 10 and about 30 percent by weight may readily be prepared by controlling the sodium to aluminum mole ratio of the sodium aluminate solution employed and the acetate to chromium mole ratio of the chromic acetate solution. The specific ratios employed will depend upon the particular composition of the chromia-alumina hydrogel desired.

Temperature, acidity, and product concentration are important variables effecting gelation and within the limits in which formation of hydrogels occurs they control gelation time. In general, the other factors can be controlled to achieve gelation at any practical solution temperature. Thus, temperatures from 30° F. to 150° F. are suitable. Best gelation times are experienced at temperatures between about 120° F. and about 140° F. The pH of the chromia-alumina hydrogels is generally between 10 and 13. For bead formation, a pH of about 12 yields excellent results.

For the production of chromia-alumina hydrogel beads, preparation is carried out substantially the same as that described in the above noted patents for producing silica-alumina beads. Thus, a chromium acetate solution and a sodium aluminate solution are contacted in a mixing nozzle and discharged onto the apex of a dividing cone from which a number of small streams flow into a column of water-immiscible liquid. The temperature of said water-immiscible liquid is desirably maintained constant by circulation through a heat exchanger outside the bead-forming tower.

The freshly formed chromia-alumina hydrogel above described is subject to a loss of aluminum as sodium aluminate is immediately washed with water. This tends to weaken the hydrogel to such an extent that it disintegrates in the wash water. That adverse effect can be avoided by immediately treating the freshly formed hydrogel in a slightly alkaline aqueous medium. This is generally accomplished by introducing the freshly formed chromia-alumina hydrogel into contact with an aqueous solution of an ammonium salt of a mineral acid or a mineral acid or a mixture of such salt and acid. In a typical operation, the freshly formed hydrogel beads are slurried out of the forming tower with oil. The hydrogel beads are then separated from the oil and treated with a 20 percent by weight solution of ammonium sulfate. The solution is advantageously kept at a pH of 8.0 to 9.5 by the addition of sulphuric acid. It is advisable to maintain a solution of this type in contact with the freshly formed hydrogel for some time after formation. For example, the solution is recirculated through the freshly formed hydrogel or otherwise maintained in contact therewith for a period of from about 2 to about 24 hours after forming in order to fix the alumina. Such treatment of the freshly formed hydrogel is designated herein as "aging."

After the aging treatment, the chromia-alumina hydrogel is water-washed free of anions introduced during aging. The washed hydrogel is thereafter ready for compositing with boria. The combination of boria with the chromia-alumina hydrogel involves intimate admixture with said hydrogel of a solid boron compound, such as borax. The composite mixture is heated by boiling until by passage of more than 1000° F. to boron oxide (B₂O₃). While boric acid, due to its availability and ease of decomposition, is preferred, other suitable boron compounds, decomposable to boron oxide under the conditions employed include boric acid esters of alcohols, such as triethyl borate and tri-methyl borate; boric acid esters of poly-hydric alcohols, such as glycerol borate and boron hydroxide, and silicate borate compounds. The boron compound is preferably in the form of a finely pulverized or powdered material. The chromia-alumina hydrogel, containing about 70 to 90 percent by weight of water, is intimately mixed with the solid boron compound in the above indicated finely divided state. Vigorous and thorough admixture of the components is necessary to achieve a homogeneous composite. It is preferred to carry out the mixing by ball-milling the hydrogel and fine particles of boron compound together for such period of time until a homogeneous composite is obtained. The mixing period will, of course, depend on the relative amounts of each of the components as well as on the total mass of material being treated. Generally, however, the mixing period will be within the range of 4 to 20 hours.

At the completion of the mixing operation, the resulting composite, either with or without intermediate formation of the same into particles, is slowly heated to an elevated temperature generally in the range of 800 to 1000° F., which temperature is sufficient to effect decomposition of the boron compound present to boria. The rate of heating should be comparatively slow, generally not in excess of 10° per minute. It is essential to the success of the present invention that the temperature to which the composite of chromia, alumina and boria is heated should not exceed about 1000° F. If such temperature is substantially exceeded, fusion of the boria component occurs with accompanying marked loss of catalytic activity. During the period of heating the wet catalyst, the atmosphere surrounding the catalyst should be desirably free of oxygen. This may be accomplished by maintaining an inert atmosphere in contact with the catalyst during the course of heating. In a preferred embodiment of the process, a non-oxidizing atmosphere may be provided by permitting the steam produced from the moisture contained in the wet catalyst to blanket the same during heat treatment. The resulting catalyst is a composite consisting essentially of chromia-alumina gel intimately combined with a catalytically effect amount of boria.

The formation, compositing and subsequent heat treatment of chromia-alumina-boria composite in accordance with this invention may be carried out either as a batch or continuous operation. Thus, the chromia-alumina hydrogel particles after formation, aging and washing may be ball milled or otherwise intimately mixed either on a batch basis or as part of a continuous operation. Heat treatment of the composited material may also be effected in a batch or continuous manner. Generally, for commercial production, it is preferred to carry out the manufacture of the catalyst in a continuous operation. A suitable continuous method of operation is shown in the form of a schematic flow diagram in Figure 1 of the attached drawing.

Referring more particularly to Figure 1, a mixing nozzle 10 into which are conducted aqueous streams of sodium aluminate and chromic acetate, is mounted over a conical divider 11 which is located near the surface of the water-immiscible liquid in forming tower 12. The colloidal solutions from which the hydrogel particles are formed are mixed and admitted through nozzle 10 to the top of the divider 11 which generally is fluted and serves to divide the stream of hydrogel into a plurality of smaller streams which enter the column of water immiscible suspending liquid in tower 12 as small droplets. The length of the column of suspending liquid and the gelation time of the sols are so regulated that the droplets will gel before passage through of less than 1000° F. to boron oxide (B₂O₃). While boric acid, due to its availability and ease of decomposition, is preferred, other suitable boron compounds, decomposable to boron oxide under the conditions employed include boric acid esters of alcohols, such as triethyl borate and tri-methyl borate; boric acid esters of poly-hydric alcohols, such as glycerol borate and boron hydroxide, and silicate borate compounds. The boron compound is preferably in the form of a finely pulverized or powdered material. The chromia-alumina hydrogel, containing...
section wherein loosely held oil drains from the particles into collecting pan 17. The oil so collected, thereafter passes through conduit 18 and is recycled to forming tower 12 by way of pump 19 and conduit 20. The hydrogel particles on the conveyor which have been drained of loosely held oil pass into the flushing section and there are flushed or reswelled with a suitable washing fluid through a spray 21. The resulting mixture of oil and washing fluid is collected in pan 22 and thereafter flows through conduit 23 to settling tank 24. The oil contained in such mixture is removed from the lower portion of tank 24 and passes through conduit 25 to pump 26 and is then recycled through conduit 20 to forming tower 12. The washing fluid separating in the upper portion of tank 24 is withdrawn through conduit 26 and recycled to spray 21 for further use in deoiling. Washing fluid make-up, as needed, is introduced through inlet 27. The chromia-alumina hydrogel particles, after being deoiled, are discharged from the conveyor belt into a flume 28 and are conducted to aging tank 29 in with the hydrogel particles are subjected to aging treatment in an aqueous media, such as an aqueous ammonium sulfate solution.

After the aging treatment, the chromia-alumina hydrogel particles are removed from tank 29 through conduit 30 and conducted to washing tank 31 in which the hydrogel particles are water-washed free of anions introduced during aging. The washed hydrogel is then removed from washing tank 31 through conduit 32 and introduced to ball mill 33. Boric acid, in finely divided particulate form, is also introduced through inlet 34 to ball mill 33. The washed chromia-alumina hydrogel and boric acid are intimately admixed in the ball mill. The ball-milled product is then conducted to an extruder 35 in which it is extruded to particles of desired size. The particles, so formed, are conducted to a kiln 36 in which the composite particles are dried and calcined at a temperature not in excess of about 1000° F. Water vapor removed from the particles passes out of the kiln through outlet 37. The product of chromia-alumina-boria catalyst passes from the kiln through outlet 38.

An alternate method of preparation of the cogelled chromia-alumina composite combined with boria as described herein involves contacting the aged, water-washed chromia-alumina hydrogel prepared as hereinafore described with an aqueous solution of a water-soluble borate compound. In this method of operation, the period of impregnation will generally be within the range of 2 to 48 hours. The impregnated composite is thereafter dried, preferably in superheated steam at a temperature of 220° to 250° F. and subsequently tempered at an elevated temperature not exceeding about 1000° F. Also, in some instances, it may be desirable to prepare the catalyst by purging the dried, tempered chromia-alumina gel particles under atmospheric pressure with steam at a temperature above 212° F., thereby replacing the air which normally occupies the gel pores with steam. The gel particles so treated may then be brought into contact with the aqueous impregnating solution of boron compound without encountering gel breakage and impregnation thereof effected. Also, it is possible to prevent gel breakage of the dried, tempered chromia-alumina gel particles by evacuating the same before contacting with the impregnating solution.

One advantage of the present catalyst over those of the prior art is that a homogeneous active catalytic surface of chromia-alumina-boria has been obtained and that the activity in reforming petroleum hydrocarbons of the result, three-component composite is distinctly improved as compared with chromia-alumina composite which had not been combined with boria. Thus, the catalyst described herein, comprising an intimate composite of aluminia, chromia, and boria in specified amounts possesses greater activity than does a corresponding composition which had not undergone combination with boria. It would appear that the advantages derived in reforming with the present catalyst are due to the specific promoting effect of the specified quantities of boria when the same are combined with chromia-alumina cogel of the above-recited composition range.

While certain details referred to in the foregoing description have been directed to catalyst preparation in which chromia-alumina gel is employed in the form of spheroidal particles, it is to be realized that it is within the purview of this invention to use chromia-alumina gels of any other desired form or shape.

The following non-limiting illustrative examples will serve more specifically to point out the process of the invention and the improved results in activity obtained with the catalyst prepared in accordance with said process.

**Example 1**

A chromia-alumina hydrogel was prepared from the following reactants:

Solution A: 47.5 pounds sodium aluminate made up to a volume of 10 gallons with distilled water;

Solution B: 48 pounds, chromic acid, the acetate to chromic ion ratio of which is adjusted within the approximate range of 2.6 to 2.8 and then made up to a volume of 13 gallons with distilled water, providing a solution containing 0.92 mole Cr₂O₃ per liter.

Solutions A and B were pumped separately under pressure through heating coils to an efficient mixing nozzle. The solutions were heated to about 110° F. and mixed at a rate of 2000 gph in equal volumes at a total rate of 1200 cc. per minute. The resulting stream of hydrogel flowed over a divider into a column of D.T.E. (diesel turbine engine) light oil. The hydrogel so formed was then washed free of exchanger between the desired product was obtained by washing the hydrogel beads were sludged from the bottom of the forming tower with a 20 percent by weight aqueous solution of ammonium sulfate. The sludged solution was maintained at a pH of 8.5 by the addition of sulfuric acid. The resulting stream of hydrogel was about 10.5, it was necessary to add sulfuric acid to the sludged solution in order to maintain the pH at 8.5. The bed hydrogel was aged for 24 hours in the same solution that was used to sludge from the forming tower. After aging, the gel was washed until a sulfate-free wash water was indicated. The washed hydrogel had a product concentration of 21 percent by weight, and contained, on a dry basis, 33.5 percent by weight chromia, 66.5 percent by weight alumina. The hydrogel was thereafter ball-milled, dried at 260 to 280° F. for 16 to 20 hours and then calcined in air for 16 hours at 1000° F.

**Example 2**

The washed chromia-alumina hydrogel prepared as in Example 1 in an amount of 3000 grams was ball-milled with 48.4 grams of powdered boric acid. The resulting composite was dried at 260 to 280° F. for 16 to 20 hours and then calcined in air for 16 hours at 1000° F. The resulting composite contained 63.4 percent by weight alumina, 31.9 percent by weight chromia, and 4.7 percent by weight boria.

**Example 3**

The catalyst of Example 1 was used in reforming a blend of 50/50 molar n-heptane and cyclohexane. The catalyst was sized to 14-25 mesh before charging to the reactor. Fifty cubic centimeters (49.84 grams) of the catalyst was placed in the catalyst zone of the reactor and activated by allowing a stream of hydrogen to pass over it at atmospheric pressure for 16 hours while holding the catalyst bed at 1000° F. In the reforming process before starting to charge the reactants to the catalyst zone, the temperature of the catalyst bed was raised to 900° F. The blend of n-heptane and cyclohexane was passed downwardly over the catalyst bed at a liquid hourly space velocity of 1. Hydrogen was mixed with the hydrocarbon feed before it entered the reactor in the ratio of 6 mols of hydrogen to 1 mol of hydrocarbon charge. The total
pressure within the system was held at 100 p.s.i.g. The reactants were passed over the catalyst during a 45 minute pre-run period, the products being discarded. Then a 30 minute balance run was made. Temperature in the cata-
lyst bed was measured by means of a movable coaxial thermocouple. During the balance run, the liquid was
catalyst and 22.5 percent fresh catalyst were used to re-
form the 50/50 molar n-heptane/cyclohexane blend, ac-
cording to the procedure of Example 3. The tempera-
tures employed were 856, 917, 969, and 1021° F.
The results of reforming in accordance with the above
Examples 3, 4, and 5 are shown in Table I below:

<table>
<thead>
<tr>
<th>Example</th>
<th>Catalyst</th>
<th>Temp., °F</th>
<th>l-C9 Yield, n-C7</th>
<th>Toluene Yield, CH,</th>
<th>CH Conversion, CH</th>
<th>MCP Yield, CH,</th>
<th>Benzene Yield</th>
<th>C9+Yield, Feed</th>
<th>C9+Yield, CH,</th>
</tr>
</thead>
<tbody>
<tr>
<td>8........</td>
<td>Chromia-Alumina Catalyst of Example 1</td>
<td>1,008</td>
<td>7.5</td>
<td>14</td>
<td>95.5</td>
<td>2</td>
<td>95</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>4........</td>
<td>Chromia - Alumina - Boria Catalyst of Example 2</td>
<td>98</td>
<td>4</td>
<td>0</td>
<td>98</td>
<td>1</td>
<td>96</td>
<td>17.5</td>
<td>10</td>
</tr>
<tr>
<td>5........</td>
<td>Catalyst of Example 2 (77.5% Regenerated from Ex. 4 and 22.5% fresh)</td>
<td>988</td>
<td>12.5</td>
<td>11.5</td>
<td>94</td>
<td>12</td>
<td>89</td>
<td>16.5</td>
<td>11.5</td>
</tr>
</tbody>
</table>

| Example | Catalyst | n-C7 Con-
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8........</td>
<td>Chromia-Alumina Catalyst of Example 1</td>
<td>18</td>
</tr>
<tr>
<td>3........</td>
<td>Chromia-Alumina Catalyst of Example 1</td>
<td>40</td>
</tr>
<tr>
<td>4........</td>
<td>Chromia - Alumina - Boria Catalyst of Example 2</td>
<td>30</td>
</tr>
</tbody>
</table>

n-C7=n-heptane.
l-C9=iso heptane.
CH=cyclohexane.
MCP=methylcyclopentane.
C9+C10=sum of hydrocarbons containing 1 or 2 carbon atoms per molecule.
C9+C18=sum of hydrocarbons containing 3 or 4 carbon atoms per molecule.

In the above Table I (Examples 3 and 4), it is clearly shown that the boria-promoted catalyst is more active for the conversion of n-heptane and cyclohexane than the unpromoted chromia-alumina. The fresh boria-promoted catalyst converted 60 percent of the n-heptane at 27° F. lower temperature than chromia-alumina. Furthermore, the addition of boria to chromia-alumina nearly doubled the yield of isohexane. At 950° F. both n-heptane conversion and cyclohexane conversion were strongly enhanced by promotion with boria. The benzene yield increased from 66 to 86 percent. Example 5 illustrates the effect of regeneration on the chromia-alumina-boria catalyst. The temperature required for conversion of 60 percent of the normal heptane was increased 7° F., while at 950° F. n-heptane and cyclohexane conversion decreased about 10 percent. Nevertheless, the regen-
erated catalyst was more active than the fresh unpromoted chromia-alumina catalyst.

Example 6

The catalyst of Example 1 was used to reform the napththa petroleum fraction having an octane number of 67 and a boiling range of between about 180 and about 390° F. The charge was reformed to 98 octane number (CFFR+3 cc. TEL), at a liquid hourly space velocity of 1, a hydrogen to hydrocarbon mole ratio of 6 and a pressure of 100 p.s.i.g.

Example 7

The catalyst of Example 2 was used to reform the same naphtha petroleum fraction under conditions identical to those set forth in Example 6.
The results of reforming, in accordance with the above Examples 6 and 7 are shown in Table II below:

<table>
<thead>
<tr>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>6........</td>
<td>Chromia-Alumina (Catalyst of Example 1)</td>
<td>963</td>
<td>83.9</td>
<td>83.4</td>
<td>75.4</td>
<td>68.5</td>
<td>0.3</td>
</tr>
<tr>
<td>7........</td>
<td>Chromia-Alumina-Boria (Catalyst of Example 2)</td>
<td>972</td>
<td>84.0</td>
<td>81.9</td>
<td>75.7</td>
<td>69.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The results of the above Table II clearly illustrate the effect of the addition of boria to chromia-alumina on the reforming catalyst activity. The boria-promoted catalyst was about 20° F. more active at 98 octane number than the unpromoted chromia-alumina. The improvement in activity of the present catalyst as compared with a chromia-alumina catalyst is shown in Figure 2 of the attached drawing. This figure shows the average temperature required to produce reformate of various octane ratings using chromia-alumina (33.5 percent Cr₂O₃, 66.5 percent Al₂O₃) and a catalyst of the present invention containing a small amount of boria in combination with the above chromia-alumina (63.4 percent by weight Al₂O₃—31.9 percent by weight Cr₂O₃—4.7 percent by weight B₂O₃).

In addition to reforming hydrocarbon mixtures falling in the gasoline range, the catalysts of the present invention are useful in catalytically promoting various other hydrocarbon conversion reactions including, by way of example, the isomerization of paraffins and dehydrogenation of napthenes. It is accordingly to be understood that the above description is merely illustrative of the preferred embodiments of the invention of which any variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

We claim:

1. A process for reforming a petroleum distillate boiling within the approximate range of 60° F. to 450° F. which comprises contacting the same at a temperature between about 700° F. and about 1000° F. at a liquid hourly space velocity between about 0.1 and about 10 in the presence of hydrogen under a pressure between about 100 and about 1000 pounds per square inch gauge and a molar ratio of hydrogen to hydrocarbon between about 1 and about 20 with a catalyst consisting essentially of chromia, alumina and boria prepared by forming a chromia-alumina hydrogel having a solids content consisting essentially of a major proportion of alumina and a minor proportion of chromia and containing between about 70 and about 90 percent by weight of water resulting from mixing aqueous solutions of sodium aluminate and chromic acetate to yield a hydrogel, controlling the sodium to aluminum ion ratio and the acetate to chromium ion ratio in said solutions to effect rapid gelation of said hydrogel to a hydrogel, aging the hydrogel obtained in a mildly alkaline aging medium, washing the aged hydrogel, intimately combining the washed hydrogel with boric acid, drying and calcining the resulting composite at a temperature not in excess of 1000° F. to yield a chromia-alumina-boria catalyst consisting essentially of 10 to 30 percent by weight of chromia, 50 to 89 percent by weight of alumina, and 1 to 20 percent by weight of boria.

2. A process for reforming a hydrocarbon mixture boiling essentially of chromia, alumina and boria prepared by forming a chromia-alumina hydrogel having a solids content consisting of a major proportion of alumina and a minor proportion of chromia and containing between about 70 and about 90 percent by weight of water resulting from mixing aqueous solutions of sodium aluminate and chromic acetate to yield a hydrogel, controlling the sodium to aluminum ion ratio and the acetate to chromium ion ratio in said solutions to effect rapid gelation of said hydrogel to a hydrogel, aging the hydrogel obtained in a mildly alkaline aging medium, washing the aged hydrogel, ball milling the said hydrogel with boric acid for a sufficient period of time to effect a resultant homogeneous product, drying and calcining the resulting composite at a temperature not in excess of 1000° F. to yield a chromia-alumina-boria catalyst consisting essentially of 24 to 30 percent by weight of chromia, 60 to 73 percent...
5. A catalyst composition consisting essentially of 10 to 30 percent by weight of chromia, 50 to 89 percent by weight of alumina and 1 to 20 percent by weight of boria, resulting from the method of preparation set forth in claim 3.

6. A catalyst consisting essentially of 24 to 30 percent by weight of chromia, 60 to 73 percent by weight of alumina and 3 to 10 percent by weight of boria, resulting from the method of preparation set forth in claim 4.