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PROCESS FOR THE TREATMENT OF HYDROCARBONS

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The present invention relates to a process for treating hydrocarbons and hydrocarbon fractions boiling in the gasoline boiling range to increase their aromaticity and improve their ignition characteristics. More particularly, the invention relates to the improvement of various hydrocarbon stocks by treatment with specific catalysts and in a specific, more economical manner.

The various commercial hydrocarbon stocks, such as those produced from petroleum oil shale, hydrogenation of coal, the catalytic cracking of heavy residuals, the polymerization of gaseous hydrocarbons, the destructive hydrogenation of gas oils, etc., which boil in the gasoline boiling range (i. e. between about 40° to 225° C.), differ widely in composition and properties depending upon their source and upon the various treatments which they may have undergone. With the exception of the coal tar distillates, most of these commercial hydrocarbon stocks contain no or relatively small proportions of aromatic hydrocarbons. Thus, although certain petroleum stocks contain minor percentages of aromatic hydrocarbons and in exceptional cases, such as in certain stocks derived from certain Borneo crudes the aromatic content is quite high, petroleum stocks usually consist completely of aliphatic hydrocarbons or a mixture of aliphatic and naphthenic hydrocarbons in various proportions. The hydrocarbons produced in the so-called Fischer and Tropsch synthesis from carbon monoxide and hydrogen are also practically entirely of an aliphatic character.

These various hydrocarbon stocks find a wide application in various fields such, for instance, as solvents, starting materials for organic synthesis and, especially, as fuels for internal combustion engines. For most of these uses it is known that hydrocarbon fractions containing an appreciable amount of aromatic hydrocarbons are much superior. Thus, for example, hydrocarbon fractions containing a substantial proportion of aromatic hydrocarbons have, in general, much better ignition characteristics and yield more power per given volume of fuel; they are also, in general, much better solvents for resins, oils, nitro-cellulose, etc. In such cases where the cost warranted, it has been the practice to add aromatic hydrocarbons. Since, however, the coal tar distillates are relatively expensive, this is in general uneconomical and can be resorted to only in special cases. For these reasons it would be very desirable to have an economical process whereby the aromatic hydrocarbons are formed in the various hydrocarbon stocks at the expense of other, less desirable hydrocarbons.

As is well known, the various hydrocarbons upon being subjected to elevated temperatures tend to revert to hydrocarbons such as aromatic hydrocarbons, the lower olefines, acetylene, methone and the like, which have greater thermal stability. As a consequence, aromatic hydrocarbons are formed to a certain extent in certain of the processes, such as reforming, dehydrogenation, thermal cracking, etc., to which the hydrocarbon stocks are commonly subjected. Although small amounts of aromatic hydrocarbons are formed by these thermal treatments, and the properties of the hydrocarbon stocks are often improved, these processes have many inherent disadvantages and are very inefficient from the present standpoint.

In view of the very limited results which may be obtained by thermal methods, it has been the aim of those skilled in the art to effect the desired improvement catalytically. It is known that certain catalysts are capable of converting naphthenic hydrocarbons to aromatic hydrocarbons by dehydrogenation; it is also known that certain catalysts, such, in particular, as chromium oxide, possess the ability to catalyze the formation of aromatic hydrocarbons from straight chain paraffin and olefin hydrocarbons by cyclization-dehydrogenation. The main difficulty hitherto encountered with catalytic methods for increasing the aromaticity of hydrocarbon stocks is in maintaining and regenerating the activity of the catalyst in a commercially practical manner. Chromium oxide, for example, while it is an active and relatively inexpensive catalyst for the process, is unsuitable for commercial use. This catalyst, even when employing pure close-cut hydrocarbon fractions, very quickly loses its catalytic activity, and the deactivated catalyst requires a time-consuming and delicately controlled reactivation treatment which is impractical in commercial operation.

The object of the present invention is to provide a method for the treatment of various hydrocarbons and hydrocarbon stocks which may be economically employed in commercial, large scale practice. In the process of the present invention the conversions are excellent, the active life of the catalyst is considerably greater than hitherto obtainable, and the main difficulty hitherto experienced, namely the reactivation of the deactivated catalyst, is substantially overcome.

The process of the present invention is appli-

cable both to the treatment of single hydrocarbons and to various hydrocarbon fractions boiling in the gasoline boiling range. While the process may be employed for the production of relatively pure aromatic hydrocarbons from single aliphatic and/or naphthenic hydrocarbons or narrow fractions of these hydrocarbons, it is also of practical value for the treatment of various hydrocarbon stocks having a considerable boiling range.

When treating hydrocarbon stocks according to the present process, several reactions may take place to a greater or lesser extent depending upon the particular stock employed and the treating conditions. Two of the more important reactions which may take place are the cyclization and dehydrogenation of aliphatic hydrocarbons to form aromatic hydrocarbons, and the dehydrogenation of naphthenic hydrocarbons to form aromatic hydrocarbons. Aside from these main reactions, alkylated aromatic hydrocarbons may be converted to polynuclear aromatic hydrocarbons; isomerization of straight chain paraffins may occur; the shifting of olefine double bonds may occur; hydrogenation of olefine double bonds may occur; and a certain amount of desulfurization may occur. Thus, paraffinic stocks destined for use in motor fuel may be treated to improve their antiknock value and general properties, such as stability, sulfur content, etc. Paraffinic hydrocarbon fractions destined for use in cleaner's naphtha, laquer diluent, paint thinner, etc., are much improved by the present treatment. The present process is especially advantageous for the treatment of naphthenic stocks to produce highly aromatic stocks which are especially suitable for blending in aviation fuel, solvents, etc. When treating a highly naphthenic stock, such as may be obtained, for example, from certain Sumatra crudes and from certain napthenic extracts, relatively pure toluol and other aromatic hydrocarbons which are suitable for use in the manufacture of explosives, etc., may be produced in large quantities at a low cost.

Aromatic stocks may also be improved by the present treatment. Hydrocarbon stocks containing small or subdominant proportions of aromatic hydrocarbons may be treated just as more aliphatic or naphthenic stocks and their aromatic content increased. Even stocks consisting predominantly of aromatic hydrocarbons, unless chemically pure, may be improved. Thus, the small to appreciable quantities of non-aromatic hydrocarbon impurities which are commonly present in commercial coal tar fractions may be converted to aromatic hydrocarbons and thus eliminated.

The treatment of the various applicable hydrocarbons and hydrocarbon stocks, according to the process of the present invention, is simple and well adapted for commercial, large-scale application. Thus, it is only necessary to pass the vapors of the hydrocarbon to be treated through a reaction chamber packed with catalyst and maintained under very practical reaction conditions and to periodically reactivate the catalyst in situ by a treatment with steam, e. g. at about 650° C.

The process of the present invention is executed with the aid of combination catalysts more fully described in our copending application No. 294,590, filed September 13, 1939, of which the present application is a continuation-in-part. These catalysts comprise the oxides of chromium and aluminum in the molecular ratio of from 90 to 60 atoms of chromium to 10 to 40 atoms of aluminum. The preferred catalysts also contain from about 2 to about 30 (more preferably from about 15 to about 20) atoms of an alkali metal (K, Na, Li, Rb, Cs) per each 100 molecules of the Cr-Al oxide combination.

It has been suggested to treat hydrocarbons with the aid of a chromium oxide catalyst. As pointed out, this catalyst is impractical for commercial use. It has also been suggested to treat hydrocarbons with a chromium oxide deposited in low concentrations on an alumina carrier. These catalysts are unsuited for the present process, since under the reaction conditions they act mainly to dehydrogenate saturated aliphatic hydrocarbons to undesirable olefines. It has, furthermore, been suggested to treat hydrocarbons with catalysts composed of chromium oxide gel and aluminum oxide in different ratios. These catalysts are not nearly as active as the present catalysts, have much shorter active life, and cannot be reactivated in a commercially practical manner.

When treating hydrocarbons, according to the invention, with the aid of the present catalysts, much better conversions are obtained than have been hitherto possible. The exceptional activity of the present catalysts is illustrated in Example I. In order to render an accurate appraisal of the present process possible, the various aspects of the invention are advisably illustrated by simple and unequivocal experiments carried out with single pure hydrocarbons.

Example I

A quantity of Cr-Al hydroxide having an atomic ratio of Cr/Al of 70/30 was prepared and sufficient aqueous KNO_3 solution added to produce a paste having 18 atoms of potassium for each 100 atoms of Cr-Al hydroxide. The paste was well mixed, dried for 18 hours at 150° C. and then treated for an additional four hours with hydrogen at 350° C. Normal heptane was passed over this catalyst at 465° C. and a contact time of 15.8 seconds. The conversion of normal heptane to aromatic hydrocarbons in a period of 46 hours of continuous operation was 31%.

In any catalytic process, such as the present, it is necessary for purely economical reasons to periodically reactivate the catalyst when its activity has declined to below an arbitrarily set minimum. Consequently, the ratio of the on-stream period to the reactivation period is of great practical importance. It has been, in fact, largely the low value of this ratio which has prevented the economical application of the hitherto proposed catalytic reforming processes. When employing the present catalysts and the simple reactivation method which may be employed therewith, this ratio is especially high. This is due both to the longer applicable onstream periods and to the shorter reactivation periods. The more favorable on-stream periods applicable to the present catalysts are illustrated in Example II.

Example II

Normal heptane was passed over various chromium oxide-containing catalysts at a temperature of 465° C. and a contact time of 15.8 seconds until the conversion to aromatic hydrocarbons declined to an arbitrarily set minimum

(20%). The on-stream periods corresponding to the various catalysts were:

Catalyst	On-stream period
	Hours
Pure Cr_2O_3	8½
Cr_2O_3-Al_2O_3 (70:30)	23
Cr_2O_3-Al_2O_3 (50:50)	16½

The usual method for the reactivation of chromium oxide catalysts is by direct oxidation of the deposited carbonaceous matter. This is generally effected by blowing a stream of oxygen or oxygen-containing gas through the bed of catalyst at a suitable temperature. The temperature must be accurately adjusted and maintained above the ignition temperature of the carbonaceous matter to be oxidized from the catalyst and below the temperature peculiar to each individual catalyst in which the catalytic activity is quickly and permanently destroyed. The control of the temperature of reactivation (usually by controlling the oxygen content and/or amount of reactivating gas) is very difficult due to the highly exothermic nature of the reaction. Another disadvantage of reactivation in this manner, which is of paramount importance from the commercial point of view, is that no materials suitable for construction of the catalytic chamber have as yet been found which are suitable and yet capable of withstanding this treatment for more than a short time. Ceramic materials do not allow sufficient heat transfer and all metal alloys so far tried catalyze the deposition of carbon after relatively few reaction-reactivation cycles.

The catalysts according to the invention are especially advantageous as regards their ability to be reactivated. With the present catalysts good conversions may be obtained with long on-stream periods (for example, an average conversion of normal heptane to toluol of 33% for an on-stream period of 46 hours); the reactivation may be effected in a more advantageous and simple manner, and the cycle may be repeated many times without serious permanent damage to the catalyst. For example, the activity of the catalyst deteriorates to about half of the original activity after about 1000 hours of use on stream. Like the hitherto proposed chromium oxide catalysts, the present catalyst may be reactivated in the usual manner with oxygen or an oxygen-containing gas, if, for any reason, this should be desired.

The present catalyst, however, unlike the hitherto proposed chromium oxide catalyst may also be reactivated in a much more efficient, economical, and easy manner by a treatment with steam, especially if they contain alkali, for example, potassium. The reactivation with steam is found to give much better results than with oxygen not only as regards the temperature control, reactor material, etc., but also as regards the reactivation itself. By simply treating the catalyst with steam, for example, at 450° C. to 850° C. the activity of the catalyst is restored substantially completely in a very short time; in fact, the first few reactivations usually increase the efficiency of the catalyst beyond that of the original fresh catalyst. It is, furthermore, found that the reactivation with steam increases the selectivity of the present catalysts to a certain extent so that the gas produced, using the reactivated catalyst, contains less undesirable contaminants.

The present catalyst may be prepared in a variety of ways. One of the essential requirements of the preparation is, however, the thorough and intimate association of the components of the combination.

Example III

Chromic oxide prepared by thermal decomposition of chromic nitrate at 200° C. was mixed with dry, very finely divided "activated alumina" in the ratio of 70 mols to 30 mols, respectively. The mixture was then thoroughly triturated in a mortar with sufficient solution of KNO_3 to produce a catalyst containing 5% K, and finally pilled.

The preparation and properties of "activated alumina" are described in U. S. Patent No. 2,184,235.

When this catalyst was employed in the cyclization of normal heptane the aromatic content of the product was 21% by weight. Although the per cent. conversion with this catalyst is low, the total yield of aromatic hydrocarbons produced per given weight of catalyst is much better than can be obtained with chromic oxide alone.

Example IV

A catalyst was prepared as described in Example III except that a chromic oxide prepared by the thermal decomposition of ammonium chromate was employed. When this catalyst was employed for the cyclization of normal heptane, the aromatic content of the product was 30%. Except for the somewhat lower average conversion afforded by these catalysts, the properties of the catalysts described in Examples III and IV are excellent.

A better method for producing very intimate contact of the chromium and aluminum oxides is by means of chemical precipitation. Thus, for instance, a hydrous oxide of chromium may be precipitated from a soluble chromium compound, such as chromic acid, a chromate, a bichromate, a trichromate, chromic nitrate, or the like. The alumina may be precipitated separately from a solution of a soluble aluminum compound and mixed with the chromium oxide. Furthermore, the two oxides may be co-precipitated from a common solution. For the preparation of the present catalysts by precipitation methods either dilute or concentrated solutions of the chromium compound and/or aluminum compound may be employed. The hydrous oxides, may, furthermore, be precipitated by any suitable base such, for example, as dilute or concentrated NH_4OH, NaOH, KOH, etc. The mixture of chromium and aluminum oxides is preferably compressed or otherwise formed into pieces of catalyst of suitable shape and size. The alkali metal compound may be incorporated in the catalyst at any convenient stage in the preparation. Prior to use, the catalyst is preferably treated for a short time with hydrogen. This pretreatment, which is not essential, is usually effected at about 300° C. to 600° C.

Inert materials such as pumice, majolica chips, diatomaceous earth, clays, carbon, and the like, may be incorporated with the hydrous oxides for the purpose of diluting, cheapening, increasing the mechanical strength of the catalyst, increasing the porosity, etc. This is illustrated by the following example:

Example V.

A solution containing chromium nitrate and aluminum nitrate in the desired proportions and containing carbon black in suspension, was precipitated with the aid of ammonium hydroxide. The precipitate containing the carbon black finely dispersed therein was filtered, washed and dried. After incorporating the desired amount of KOH and pilling, the catalyst mixture contained 10% by weight of carbon. The catalyst pills were first treated with steam at 600° C. and then at 650° C. until substantially free of carbon. In this way very active and porous catalyst pills were prepared.

The catalysts may also contain small proportions of other substances which may increase the activity, increase the catalyst life, aid in the catalyst reactivation, inhibit undesirable side reactions, or the like. Thus, for example, the catalyst may, in general, be improved to a certain extent by incorporating small quantities of promoters, such as copper compounds, thallium compounds, or the like.

While the present catalysts may be prepared as above described by any conventional methods, superior catalysts which are used in the preferred embodiment of the present invention are prepared by the special procedure more fully described in copending application No. 298,613, filed October 9, 1939. In the preparation of the preferred catalysts of the above described composition, the hydroxides of chromium and aluminum in the desired proportions are coprecipitated by continuously introducing the reagents at suitable controlled rates into a comparatively small reaction space, and the reaction mixture containing the precipitated hydroxides is promptly subjected to a very short heat treatment. The optimum duration of the heat treatment depends somewhat upon the temperature of the treatment. Generally speaking, if the reaction mixture is heated only very mildly, for instance up to about 40° C. to 50° C., the time of heating may be prolonged to as much as about 10 minutes. It is preferable, however, to heat the reaction mixtures to somewhat higher temperatures, for instance between 50° C. and the boiling point of the reaction mixture. At these more desirable temperatures, the time of heating is preferably considerably shorter. Thus, for example, a suitable heat treatment may be from 2 to 10 seconds at about 70° C. to 100° C. After the short heat treatment, the precipitate is preferably promptly separated from the cooled reaction mixture and washed, dried, etc. in the usual manner.

The alkali metal may be incorporated in the Cr-Al hydroxide combination by mixing with the required amount of a solution of an alkali metal compound, such as the sulfate, nitrate, carbonate, hydroxide, oxide, phosphate, bicarbonate, borate, aluminate, salts of organic acids, or the like, preferably prior to drying. The halides were found to be less suitable.

The catalyst, according to the process of the present invention, is preferably employed in a bed consisting of pieces of a size and shape suitable for vapor phase reactions and the gaseous hydrocarbon passed thereover. While pressures both below and somewhat above atmospheric pressure are applicable, the process is preferably executed in practice at atmospheric pressure or thereabouts (for instance, from about 1 to 10 atmospheres). The reaction chamber containing the catalyst is preferably maintained at a reaction temperature between about 400° C. and 600° C. Temperatures lower than about 400° C. are in general, less desirable, since they require low space velocities and give low conversions. Temperatures above about 600° C. allow much higher space velocities and high conversions but are, in general, less desirable since they are apt to lead to cracking and carbon deposition. At temperatures between about 450° C. and 500° C., the contact time is preferably at least five seconds. At higher temperatures somewhat higher space velocities may be employed. This is especially true when the hydrocarbon feed is diluted with hydrogen. In the presence of added hydrogen, the contact time may be decreased to less than one second, e. g. ½ second.

Example VI

Methyl cyclohexane was passed at a rate of 10 cm.^{3} per hour at 465° C. and 1 atmosphere pressure over an 18 cm.^{3} bed of catalyst. The catalyst, prepared as above described, contained aluminum oxide and chromium oxide in a mol. ratio of 30:70 and 18 atoms of potassium (in the form of potassium hydroxide) per each 100 molecules of the mixed oxides. Measured over a period of 100 hours, an average of 83% of the methyl cyclohexane was converted into aromatic hydrocarbons, mainly toluene. During this experiment the catalyst showed only a slight decrease of activity; in fact, after 100 hours the activity had decreased to 92% of its maximum value.

In order to prevent the catalyst becoming inactive owing to the deposition of carbonaceous products it has been found effective to operate in dilution with hydrogen. Favorable amounts of hydrogen are, for example, 5 to 25 mols per mol. hydrocarbon.

The effect of the hydrogen can be improved by working under pressure. Very good results are obtained at hydrogen partial pressures ranging between 2 and 6 atm.

Under these circumstances it is possible to operate at higher temperatures than in the past, viz. at temperatures between about 500 and 575° C. An advantage of these high operating temperatures is that they approach the reactivation temperatures used during the reactivation period with steam, thus avoiding substantial changes in the temperature when switching over from dehydrogenation-cyclisation to reactivation and vice versa, which, in the long run would unfavorably affect the material from which the apparatus is constructed.

Example VII

A fraction of a Venezuelan straight-run gasoline containing naphthenes having pentamethylene rings and boiling between 85 and 104° C. was forced at a rate of 1 liter per hour and under a pressure of 15 atmospheres, together with 4% by weight of hydrochloric acid, through a 2-liter stirrer autoclave, which contained 500 g. aluminum chloride. The autoclave was kept at a temperature of 80° C.

The reaction product formed was washed with lye and water to remove the aluminum chloride and hydrochloric acid, and thereafter dried and distilled, the fraction boiling up to 125° C. being collected. In the gasoline mixture thus obtained the naphthenes having pentamethylene rings which are detrimental to the catalyst, are substantially converted into 6-ring naphthenes.

This fraction was passed with a throughput of 0.38 kg. per liter of catalyst per hour over a catalyst consisting of a mixture of 30 mol. % Al_2O_3 and 70 mol. % Cr_2O_3, compressed to grains of about 5 mm. diameter, and also containing 4½% by weight potassium in the form of KNO_3. In admixture with the gasoline fraction hydrogen was passed over the catalyst at a rate of 2400 liters per kg. gasoline fraction.

The total pressure was 5 atmospheres and the partial pressure of the hydrocarbons was 0.45 atmosphere.

The reaction temperature during the first six hours was 525° C., during the following six hours 540° C. and during the last six hours 560° C.

The initial gasoline fraction consisted of 6% by weight aromatics, 40% by weight paraffins and 54% by weight naphthenes.

During the first six hours a liquid reaction product was obtained in a yield of 92%, calculated on intake, which consisted of 79% by weight aromatics, 5% by weight olefines and 16% by weight paraffins containing a few naphthenes having pentamethylene rings.

During the following six hours a liquid product was obtained in a yield of 86% by weight, consisting of 83% by weight aromatics, 5% by weight olefines and 12% by weight paraffins containing a few naphthenes having pentamethylene rings.

During the last six hours a liquid reaction product was obtained in a yield of 79% by weight, consisting of 82% by weight aromatics, 5% by weight olefines and 13% by weight paraffins containing a few naphthenes having pentamethylene rings.

The catalyst was then regenerated by steaming during three hours at 650° C. and recovered its original activity.

Example VIII

750 g. of a Borneo gasoline, boiling between 85 and 104° C. and consisting of 74% by weight naphthenes, 3% by weight aromatics and 23% by weight paraffins, was treated for 10 hours at 80° C. in a 2-liter rotating stainless steel autoclave with 40 g. $AlCl_3$ and 100 g. HCl, such with a view to converting the greater part, namely about 80–85%, of the naphthenes having pentamethylene rings present into naphthenes having hexamethylene rings. After removal of $AlCl_3$ and HCl with lye and water the reaction product was dried. The gasoline obtained consisted of 73% by weight naphthenes, 2% by weight aromatics and 25% by weight paraffins.

The gasoline thus pretreated was then passed of a rate of 20 $cm.^3$ per hour together with a 10 molar quantity of hydrogen (about 2400 1 per kg. gasoline) and at an absolute pressure of 6 atmospheres over 36 $cm.^3$ of a catalyst in the form of tablets of about ½ cm. diameter consisting of a mixture of 30 mol. % Al_2O_3 and 70 mol. % Cr_2O_3, obtained through the co-precipitation of the hydroxides, to which precipitated mixture 16 atoms of potassium (in the form of potassium hydroxide) had been added per 100 mols oxide mixture.

During the first 18 hours the reaction temperature was 525° C., during the following 9 hours 535° C. and during the next 6 hours 545° C. The catalyst was then regenerated by passing over steam during 5 hours at 650° C. and at an absolute pressure of 6 atmospheres. The catalyst thus recovered its original activity.

The reaction products obtained during the three runs were added together. From 498 g. initial material (gasoline treated with $AlCl_3$ and HCl) a total yield of 447 g. liquid product was thus obtained, which product consisted of 17% by weight naphthenes, 68% by weight aromatics, 10% by weight paraffins and 5% by weight aliphatic olefines.

The above examples, which illustrate various aspects of the invention, are not to be construed as limiting the invention. It is to be understood that modifications will be apparent to those skilled in the art and that no limitations are intended other than those imposed by the scope of the appended claims.

We claim as our invention:

1. A process for the production of aromatic hydrocarbons which comprises the steps of passing vapors of a naphthenic hydrocarbon boiling within the gasoline boiling range, at a temperature of from 400° to 600° C., over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40 and a non-halogen-containing alkali metal compound in an amount corresponding to from 2 to 30 atoms of alkali metal per each 100 molecules of said mixed oxides, and periodically interrupting the flow of hydrocarbon gases and restoring the catalytic activity of the catalyst by a treatment with steam at a temperature between 450° C. and 850° C.

2. A process for improving hydrocarbon distillates which comprises the steps of passing vapors of a hydrocarbon fraction distilling within the gasoline boiling range at a temperature of from 400° to 600° C., over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40 and a non-halogen-containing alkali metal compound in an amount corresponding to from 2 to 30 atoms of alkali metal per each 100 molecules of said mixed oxides, and periodically interrupting the flow of hydrocarbon gases and restoring the catalytic activity of the catalyst by a treatment with steam at a temperature between 480° C. and 850° C.

3. A process for the production of aromatic hydrocarbons from naphthenic hydrocarbons which comprises the step of passing vapors of a naphthenic hydrocarbon distilling within the gasoline boiling range, at a temperature of from 400° to 600° C., over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40 and an alkali metal compound in an amount corresponding to from 2 to 30 atoms of alkali metal per each 100 molecules of said mixed oxides.

4. A process for the production of aromatic hydrocarbons from naphthenic hydrocarbons which comprises the step of passing vapors of a naphthenic hydrocarbon distilling within the gasoline boiling range, at a temperature of from 400° to 600° C., over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40.

5. A process for improving hydrocarbon distillates which comprises the step of passing vapors of a hydrocarbon fraction distilling within the gasoline boiling range, at a temperature of from 400° to 600° C., over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40 and an alkali metal compound in an amount corresponding to from 2 to 30 atoms of alkali metal per each 100 molecules of said mixed oxides.

6. A process for improving hydrocarbon distillates which comprises the step of passing vapors

of a hydrocarbon fraction distilling within the gasoline boiling range, at a temperature of from 400° to 600° C., over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40.

7. A process for improving hydrocarbon distillates which comprises the step of passing vapors of a hydrocarbon fraction distilling within the gasoline boiling range together with hydrogen at a temperature of from 400° to 600° C. over a solid catalyst comprising chromium oxide and aluminum oxide in a molecular ratio from 90:10 to 60:40 and an alkali metal compound in an amount corresponding to from 2 to 30 atoms of alkali metal per each 100 molecules of said mixed oxides.

8. A process for improving hydrocarbon distillates which comprises the step of passing vapors of a hydrocarbon fraction distilling within the gasoline boiling range together with hydrogen of a partial pressure between 2 and 6 atmospheres at a temperature exceeding 500° C. over a solid catalyst comprising chromium oxide and aluminum oxide in a molecular ratio from 90:10 to 60:40 and an alkali metal compound in an amount corresponding to from 2 to 30 atoms of alkali metal per each 100 molecules of said mixed oxides.

9. A process for the production of aromatic hydrocarbons from aliphatic hydrocarbons which comprises passing vapors of an aliphatic hydrocarbon boiling within the gasoline boiling range over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40 at a temperature of from 400° C. to 600° C.

10. A process for the production of aromatic hydrocarbons from aliphatic hydrocarbons which comprises passing vapors of an aliphatic hydrocarbon boiling within the gasoline boiling range over a solid catalyst comprising coprecipitated chromium oxide and aluminum oxide in a molecular ratio of from 90:10 to 60:40, and an alkali metal compound in an amount corresponding to from 2 to 30 atoms of alkali metal per each 100 molecules of said mixed oxides at a temperature of from 400° C. to 600° C.

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