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12/19/2001 10:04:24



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(12) Patent:

(54) AROMATIC HYDROCARBON SYNTHESIS

(54) SYNTHESE D'HYDROCARBURES AROMATIQUES

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407150

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN, that we, GERARDUS HENDRICUS VISSER and WILLEM FREDERIK ENGEL, subjects of the Queen of The Netherlands and residents of Amsterdam, The Netherlands, have invented a new and useful improvement in the

SYNTHESIS OF AROMATIC HYDROCARBONS

of which the following is a full, clear and exact specification.

The present invention relates to the synthesis of aromatic hydrocarbons from open chain hydrocarbons with the aid of certain especially adapted catalytic agents.

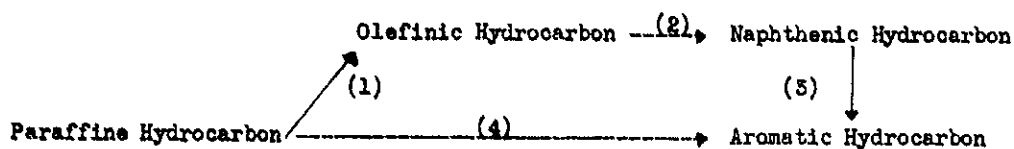
An object of the invention is to provide a commercially practical process for the synthesis of valuable aromatic hydrocarbons from readily available and inexpensive saturated and unsaturated hydrocarbons having preferably not more than 12 carbon atoms in an open chain and structurally capable of being cyclised to six-membered rings. A further object of the invention is to provide certain specific catalytic agents which upon careful and extensive investigation have been found to be exceptionally suitable and superior to previously disclosed catalyst preparations for the above purpose.

Of the various classes of hydrocarbons, the paraffins, and next the olefines, especially those of high molecular weight, are, generally speaking, the least stable to heat. These hydrocarbons, either alone or in various complex hydrocarbon mixtures, therefore tend, upon being subjected to elevated temperatures, to revert to hydrocarbons having greater thermal stability such as methane, aromatic hydrocarbons, the lower olefines, acetylene, and the like. As a consequence, aromatic hydrocarbons are formed to a certain extent in many of the numerous processes, such as reforming, dehydrogenation, thermal cracking, catalytic cracking, etc., to which the liquid, open chain hydrocarbons, usually in the form of petroleum stocks, are commonly subjected. Although small amounts of aromatic hydrocarbons are formed in certain of these processes when applied to particular hydrocarbon stocks, the formation of aromatic hydrocarbons is not the primary reaction and, furthermore, does not take place, in general, to any appreciable extent by synthesis from open chain hydrocarbons.

Thus, for example, in the reforming of certain petroleum fractions over metal oxide catalysts, the antiknock properties are improved, and it is often stated that the aromatic content is increased. The increase of the aromatic content sometimes noticed in the reformed stocks treated in the presence of the dehydrogenation catalysts usually employed is, however, due primarily to the dehydrogenation of naphthenic hydrocarbons present in the raw stock and the increase in the antiknock properties is due to a large extent to the production of high antiknock olefines by dehydrogenation.

The present process, although it is well adapted to increase the aromatic content and improve the antiknock properties of petroleum fractions, is not to be considered as a simple reforming process, or the like, but as a process for the production of aromatic hydrocarbons. In the present process, the aromatic hydrocarbons are not formed in small amounts by secondary reactions, nor primarily by the dehydrogenation of naphthenic hydrocarbons, but are formed almost exclusively in practical quantities by direct synthesis from open chain hydrocarbons.

The formation of aromatic hydrocarbons from saturated hydrocarbons containing at least six carbon atoms in an open chain can take place by at least two mechanisms.



The direct conversion of saturated aliphatic hydrocarbons to aromatic hydrocarbons according to reaction (4) takes place, in general, to an appreciable extent only when quite high temperatures are employed. Reactions (1) and (5) are simple dehydrogenation reactions which, as is known, can be accelerated by means of a large number of catalysts. The rate of reaction (2) is, however, normally very slow and is, in general, not accelerated to any appreciable extent by most of the usual catalysts proposed for catalytic reforming, dehydrogenation and similar hydrocarbon treatments. Thus, for example, the oxides of iron, cobalt, nickel, vanadium, titanium, and the like,

which have been repeatedly proposed for treating hydrocarbons, primarily affect the C-H bond and act as dehydrogenation catalysts. When petroleum fractions are treated at elevated temperatures in the presence of such catalysts, any naphthenic hydrocarbons present in the raw stock are dehydrogenated to aromatic hydrocarbons and paraffine hydrocarbons are dehydrogenated to an appreciable extent to olefines, but very little, if any, aromatic hydrocarbons are formed by cyclization via reaction (2). Most of these catalysts also act as hydrogenation catalysts and, under the conditions most commonly employed, considerable destructive hydrogenation and/or polymerization of the olefinic hydrocarbons formed also takes place simultaneously.

As will be apparent from the above, catalysts which selectively affect the C-H bond and act primarily as hydrogenation and/or dehydrogenation catalysts are not the most suitable for the production of aromatic hydrocarbons by cyclization. In order to produce appreciable quantities of aromatic hydrocarbons in a practical temperature range via reactions (1), (2), and (5), it is desirable to employ a catalyst which catalyzes both dehydrogenation (Reactions (1) and (5)) and cyclization (Reaction (2)) and is so balanced that the rates of reactions (1) and (2) are as nearly equal as possible. If the rate of reaction (1) greatly exceeds that of reaction (2), large amounts of free olefines are formed. This is undesirable both in the direct production of aromatic hydrocarbons and in the reforming of petroleum distillates, since in the former it leads to low yield and undesirable polymer formation, and in the latter it tends to give distillates which suffer high losses in refining and are less stable on storage.

The property of catalyzing the cyclization reaction (2) is possessed only by a relatively few materials practically restricted to the oxides of the metals on the left hand side of Group VI of the Periodic System of the Elements. Of these metal oxides, chromium oxide is by far the most active. Although the production of aromatic hydrocarbons through cyclization with the aid of this catalyst has been the subject of considerable study, the results have remained primarily of academic interest and no commercially practical process has hitherto resulted.

We have found certain superior combination catalysts which give high conversions to aromatic compounds, produce practically no olefines and relatively pure hydrogen, have exceptionally long active life, and can be efficiently and repeatedly reactivated in a most simple and practical manner. These catalysts are composed essentially of oxides of chromium and aluminum in certain ratios and in intimate association. We have, moreover, found that these catalyst combinations are further considerably improved by the presence of certain quantities of alkali metal compounds.

The combination chromium oxide-alumina catalysts, which we have found to be especially suitable for catalyzing the production of aromatic hydrocarbons from open chain hydrocarbons, contain chromium oxide and aluminum oxide in molecular ratios of from 90 to 60 atoms of chromium to 10 to 40 atoms of aluminum. If it is assumed for the purpose of calculation that the aluminum exists in the catalyst in the form of Al_2O_3 and the chromium as Cr_2O_3 , this corresponds to from about 7% to about 31% by weight of aluminum oxide in the chromium oxide-alumina mixture. The distinct superiority of the present combination catalysts and the effect of the ratio of the components are illustrated in the following example:

EXAMPLE I

A series of combination Cr-Al oxide catalysts containing various ratios of Cr/Al were prepared by continuously introducing solutions of a chromium compound, solutions of an aluminum compound, and a solution of ammonia in the desired proportions into a mixing chamber. The precipitated products were heated for a short time at $97^{\circ}C.$, cooled to $25^{\circ}C.$, filtered, washed with water, dried for two hours at $105^{\circ}C.$ in a drying oven and finally treated at $550^{\circ}C.$ for four hours in a stream of hydrogen. The resultant oxide products were pressed into pastilles of 5 mm diameter and 4.5 mm thickness and placed in equal volume amounts in a suitable catalyst tube mounted in an electrically heated furnace. In separate and comparable experiments pure normal heptane was passed over each of the catalysts at a temperature of $465^{\circ}C.$ and a contact time of 15.8 sec. The yields of aromatic hydrocarbons (predominantly toluene)

corresponding to the catalysts containing different atomic ratios of Cr/Al under these conditions are shown graphically in Figure I of the attached drawing. The pronounced superiority of the present combination catalysts having atomic ratios of Cr/Al of from about 90/10 to about 60/40 and the great influence of this ratio are clearly seen upon inspection of the graph.

The curve of Figure I, shows the yields of aromatic hydrocarbons at the end of 15 hours of continuous use. The decided superiority of these catalysts is even more pronounced if the total average yield of aromatic hydrocarbons, taken for the total time of use, is considered. This is shown in Figure II of the attached drawing wherein the weight per cent of normal heptane converted to aromatic hydrocarbons over a period of 31 hours of continuous operation is plotted against the composition of the catalyst. Since the density, cost, and chromium content of the catalyst decrease with decreasing ratios of Cr/Al, the results shown in these graphs are in reality even better than it would appear since they are all based on experiments using equal volumes of catalyst.

In such processes as the present, it is necessary, for purely economical reasons, to reactivate the catalyst as soon as its activity falls below an arbitrarily set minimum. The applicable "on stream period" which may be employed with any catalyst before it is necessary to undergo reactivation is, therefore, of great practical importance. Although some of the previously proposed catalysts are capable of being reactivated, they require excessive time for reactivation, i.e. the ratio of the "on stream time" to the "reactivation time" is low. The time required for the yield of aromatic hydrocarbons to depreciate to an arbitrarily set conversion of 20% in the above-described experiments is shown graphically in Figure III. It is seen from this graph that whereas pure chromium oxide catalyst deteriorated in 8-1/2 hours and a catalyst consisting of chromium oxide and alumina in the molecular ratio of 1:1 deteriorated in 16-1/2 hours, the catalysts of the present invention containing the chromium oxide and alumina in the molecular ratios of 90/10 to 60/40 maintained a conversion above 20% for as long as 25 hours.

The distinct superiority of the present catalysts is quite remarkable and unique and is practically restricted to these particular combinations of the oxides of chromium and aluminum. If the chromium oxide is replaced by oxides of Fe, Co, Ni, Mn, Mo, or other metal oxides known to exert a strong dehydrogenation action, for example, the catalyst is found to act primarily as a dehydrogenation catalyst and little or no aromatic hydrocarbons are formed by cyclization. Also, on the other hand, the effect of the alumina is quite unique and is not an equivalent of other related oxides. This is clearly shown in the following table showing results obtained upon treating normal heptane with various catalyst combinations containing chromium oxide:

TABLE I

<u>Catalyst</u>	<u>Conversion in % by Weight</u>		
	<u>After 4-1/2 hours</u>	<u>After 13-1/2 hours</u>	<u>% Depreciation</u>
$\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$	42	29	51
Cr_2O_3	54	11.5	69
$\text{Cr}_2\text{O}_3\text{-ZnO}$	55	18	45
$\text{Cr}_2\text{O}_3\text{-ThO}_2$	52	10	69
$\text{Cr}_2\text{O}_3\text{-B}_2\text{O}_3$	50	17	45
$\text{Cr}_2\text{O}_3\text{-BaO}$	28	6	79

The reason for the pronounced maximum activity of the present catalyst combinations containing chromium oxide and alumina in these particular ratios has not been definitely established. It is known that various metal oxides such as those of Zn, Si, Th, Ti, B, etc., are able to stabilize the structure of certain especially prepared vitreous chromic oxide gels claimed to be suitable for catalyzing hydrogenation and dehydrogenation reactions. This, however, relates to the stabilizing of a special form of chromium oxide against structural deformation by heat rather than an improvement in the catalytic properties. This stabilizing effect is, furthermore, produced by a wide range of ratios of a variety of metal oxides and is not confined to a narrow range of concentrations of aluminum oxide. While we do not desire our invention

to be limited in any manner by the soundness or accuracy of any theories advanced to explain the advantageous results obtained, it is believed that the marked superiority of the present catalysts for the synthesis of aromatic hydrocarbons from open chain hydrocarbons is due not only to a proper balance of the dehydrogenation and cyclization activities, but also to the formation during use of mixtures containing certain lower oxide forms in the most efficient ratio. The fact that catalytically active lower oxide forms are produced in the catalyst combination during use has been definitely proven.

While the above-described binary mixtures constitute a class of superior catalysts for the conversion of open chain hydrocarbons to aromatic hydrocarbons, the preferred catalysts of the present invention are those of a more complex type which contain alkali metal compounds.

The presence of certain quantities of alkali metal atoms in the catalyst, it is found, increases the yield of aromatic hydrocarbons formed, increases the reactivity of the catalyst for the production of aromatic hydrocarbons, increases the life of the catalyst, and materially aids in the catalyst reactivation. The effect of certain quantities of alkali metal compounds in these respects is quite different than might be expected. For example, if a potassium compound is added to pure chromium oxide catalyst, it is found that amounts greater than about 1% K destroy the cyclizing ability of the catalyst almost completely. In the case of the present chromium oxide-alumina catalysts, however, the effect of the presence of alkali metal compounds is exactly the opposite. In the present catalyst compositions very small amounts of alkali metal compounds exert a slight inhibiting effect and larger amounts have a very beneficial effect. The effect of alkali metal in the present catalyst compositions is clearly shown by the following example:

EXAMPLE II

A quantity of Cr/Al hydroxide having an atomic ratio of Cr/Al of 70/30 was prepared. To portions of the Cr/Al hydroxide there were added sufficient amounts of aqueous KNO_3 solutions of suitable concentrations to produce pastes having the desired potassium content. The pastes were stirred until they were

of even consistency, dried for 18 hours at 150°C., and then treated for an additional four hours with hydrogen at 350°C. The various catalysts so prepared (containing 0.00, 0.3, 0.65, 1.0, 1.5, 1.7, 2.1, 2.5, 3.5, 4.6, 5.0, 5.5, 6.0, and 8.0 per cent of potassium) were employed under identical conditions for the cyclization of n-heptane at 465°C. and a contact time of 15.8 sec. The yields in per cent by weight of heptane converted to aromatic hydrocarbons in a period of 46 hours of continuous operation are shown graphically in Figure IV in the accompanying drawing.

Whereas the beneficial effect of the combination of chromium and aluminum oxides appears to be practically limited to this particular combination, the effect of alkali metal compounds is found to be general to the alkali metals of Group I of the Periodic System. While K, Na, Rb, and Cs all show the same beneficial effects, the effect of potassium is somewhat more pronounced and this material is therefore preferred.

The amount of alkali metal compound incorporated into the Cr/Al oxide is preferably adjusted to give catalyst combinations which are the most effective in the cyclization process. In general, amounts of alkali metal compound ranging from about 15 to 20 alkali metal atoms per each 100 molecules of the Cr/Al oxide combination are found to give the best results. Amounts ranging from 2 to about 50 alkali metal atoms are, however, often advantageous and may be employed.

The alkali metal may be incorporated in the form of alkali metal compounds such, for instance, as sulfates, nitrates, carbonates, hydroxides, oxides, phosphates, bicarbonates, borates, aluminates, salts of organic acids, and the like. The substantial equivalency of some of the various anions is illustrated by the following example:

EXAMPLE III

A series of Cr/Al oxide catalysts (70:30) containing 2-1/2% K in the form of various potassium compounds, was prepared. The catalysts were tested for their activity in the cyclization of normal heptane at 465°C. and 15.8 sec. contact time under comparable conditions. The results were as follows:

TABLE II

Per cent by Weight of Normal Heptane
Converted to Aromatic Hydrocarbons.

<u>K Compound Applied</u>	<u>After 4-1/2</u> <u>hours</u>	<u>After 28-1/2</u> <u>hours</u>
KOH	46	26
KNO ₃	41	22
K ₃ PO ₄	40	24
K ₂ CO ₃	45	23
K ₂ SO ₄	42	22

The approximate equivalency of the various compounds of the alkali metals is due, no doubt, to the fact that they change to other forms (or even to a common form) during the use of the catalyst. Generally speaking, the alkaline-reacting water soluble compounds of the alkali metals, such as the hydroxides in particular, give excellent results, and are more desirable from a technical point of view since they are, in general, easily incorporated in the catalyst, inexpensive, noncorrosive, and do not generate harmful vapors during use. The nitrates, however, are somewhat more advantageous in certain other respects. The catalyst pills prepared using KOH, for example, are of exceedingly loose structure, whereas those prepared using an equivalent amount of KNO₃ and compressed under the same pressure are very firm. Catalysts prepared using KNO₃ also show a somewhat higher activity after regeneration. The chlorides, sulfides and salts of strong oxidizing acids such, for instance, as the bichromates, are somewhat less preferred.

The presence of alkali metal atoms in the present catalysts not only increases the efficiency of the Cr-Al oxide combination for catalyzing the production of aromatics but also increases the selectivity of the catalyst. Thus, the gas produced when employing alkali-containing catalysts is less contaminated with products of side reactions and consists almost entirely of hydrogen. The gas produced when cyclizing normal heptane with the aid of the above described catalyst containing 5% K, for example, analyzed:

94% H₂

1% Unsaturated hydrocarbons

5% Saturated hydrocarbons

The present catalysts 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 IV

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. This mixture was then thoroughly triturated in a mortar with sufficient solution of KNO₃ to produce a catalyst containing 5% K, and finally pilled.

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 V

A catalyst was prepared as described in Example IV 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 50%. Except for the somewhat lower average conversion afforded by these catalysts, the properties of the catalysts described in Examples IV and V 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 300-600°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 VI

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 present catalysts containing oxides of chromium and aluminum in suitable ratios and preferably containing an alkali metal compound may also, if desired, 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. The incorporation of 6% of CuO in a catalyst containing potassium equivalent to 6% K_2O , for example, increases the conversion to aromatic hydrocarbons by about 1 to 2%.

In order for any catalyst of the present type to be economically practical, it must of necessity be capable of simple and repeated reactivation. Although chromium oxide itself possesses a fair ability to catalyze cyclization reactions and can be reactivated, the catalytic cyclization activity drops so fast that it can be used only for very short periods between reactivations. As a consequence, the time that the catalyst is "on reactivation" considerably exceeds that of the productive "on stream period". Furthermore, pure chromium oxide catalysts are permanently damaged during use so that each succeeding reactivation is less complete, and after only a very few reactivations the catalyst can no longer be profitably reactivated and must be replaced. The reactivation is generally effected by blowing a stream of oxygen or oxygen-containing gas through the bed of catalyst in situ 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 at 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 a relatively few reaction-reativation cycles.

The present catalysts, especially those containing from about 1 to 5% of an alkali metal, are exceptionally advantageous as regards their ability to be reactivated. With the present catalysts good average conversions may be obtained with exceptionally long on stream periods, (for example, an average conversion 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 catalysts may be reactivated in the usual manner with oxygen or an oxygen-containing gas, if for any reason this is desired. The present catalyst, however, unlike the hitherto-proposed chromium oxide catalysts, may also be reactivated in a much more efficient, economical and easy manner by a treatment with steam. The reactivation with steam is found to give much better results than with oxygen not only as regards the temperature control, tube 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 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. This is shown in the following table:

TABLE III

Analysis of Exit Gas

<u>Fresh Catalyst</u>	<u>After 2 On Stream Periods and 2 Reactivations with Steam.</u>
92.5% H ₂	95.6% H ₂
1.0% Unsaturated Hydrocarbons	0.4% Unsaturated Hydrocarbons
6.5% Saturated Hydrocarbons	4.0% Saturated Hydrocarbons

When reactivating with oxygen the above-mentioned effects are usually reversed.

The present catalysts and process are especially suitable for the production of aromatic hydrocarbons and relatively simple mixtures of aromatic hydrocarbons from individual hydrocarbons having preferably not more than twelve carbon atoms in an open chain and capable of being cyclized

to six-membered rings and/or hydrocarbon mixtures containing one or more of such hydrocarbons in appreciable quantities. Thus, the present process is applicable to the economic production of mono-nuclear aromatic hydrocarbons from hydrocarbons containing at least six and preferably not more than twelve carbon atoms in an open chain. For example, the predominant aromatic hydrocarbons found in the product when treating a few of such open chain hydrocarbons are shown in the following table:

TABLE IV

<u>Open Chain Hydrocarbon Employed</u>	<u>Predominant Aromatic Hydrocarbons Found in the Reaction Product</u>
N-Hexane	Benzene
N-Heptane	Toluene
2-Methyl Hexane	Toluene
N-Octane	Ortho Xylene
2,5-Dimethyl Hexane	Para Xylene
N-Nonane	Ortho Methyl Ethyl Benzene
N-Decane	Ortho Methyl Propyl Benzene
Hexene-1	Benzene
Hexene-2	Benzene
N-Octene	Ortho Xylene

The process is also applicable for the production of poly-nuclear aromatic hydrocarbons from alkylated aromatic and hydro-aromatic hydrocarbons, such as n-butyl benzene, n-amyl benzene, n-butyl cyclohexane, crotyl benzene, and the like. Of the various applicable hydrocarbons we have found that, in general, somewhat better results are obtained with normal and slightly branched hydrocarbons and that olefinic hydrocarbons are converted somewhat more easily than their saturated analogues. Applicable hydrocarbon mixtures may also contain higher and/or lower boiling cyclizable and noncyclizable hydrocarbons, naphthenic hydrocarbons, paraffinic hydrocarbons, olefinic hydrocarbons, and the like. Thus, for example, normal heptane has been cyclized in the presence of methane, propane, propylene, benzene, toluene, iso-octane, and 2-methyl pentane, and excellent yields of toluene obtained.

The process is suitable for the conversion of paraffinic and olefinic hydrocarbons in light petroleum fractions, such as gasoline, etc., into aromatic hydrocarbons. By treating such petroleum fractions according to the present process, their aromatic content is considerably increased (any hydro-aromatic hydrocarbons which may be present are also dehydrogenated to aromatic hydrocarbons), very little cracking occurs and a stable product of low olefine content and increased antiknock properties is obtained. Peroxides have been found to be very detrimental in the process. Olefines and/or olefinic stocks, if employed, are preferably substantially peroxide-free.

The hydrocarbon or hydrocarbon mixture to be treated according to the present process is preferably passed as a vapor through a bed of the catalyst supported in a suitable converter and maintained at the desired temperature by any suitable heating means. While pressures both below and somewhat above atmospheric pressure (for instance 1 to 5 atm.) are applicable, the process is preferably executed in practice at atmospheric pressure or thereabouts. The hydrocarbon to be treated is preferably substantially free of water and/or compounds, such as the alcohols which form water under the reaction conditions.

In order to produce the best yields of aromatic hydrocarbons and realize the maximum efficiency of the catalyst, the temperature in the catalytic converter is preferably maintained between about 400 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° and 500°C. the contact time is preferably at least five sec. At higher temperatures somewhat higher space velocities may be employed, especially by diluting the feed with hydrogen the contact time may then be decreased even to less than one second, e.g. 1/2 second.

EXAMPLE VII

Normal nonane was passed at a rate of 20 cm^3 (14.35 gm.) per hour at 465°C . and atmospheric pressure over 40 cm^3 (37 gm.) of compressed catalyst pills of about 5 mm consisting of a mixture of chromium oxide and aluminum oxide in a molecular ratio of 70:30 and 18 atoms of potassium (added in the form of KOH) per each 100 molecules of the mixed oxides. The liquid reaction product obtained during a period of 10 hours amounted to 83% by weight of the initial material and contained:

71% by weight of aromatic hydrocarbons

6% by weight of olefines

23% by weight of paraffins

The aromatic hydrocarbon fraction consisted of about 80% by weight of ortho-methyl ethyl benzene.

The hydrocarbon product obtained, according to the process, may be treated by any one of the many known methods to remove the aromatic hydrocarbons formed in the treatment, or, if desired, non-aromatic hydrocarbons may be removed leaving a concentrated aromatic fraction. In many cases, especially when operating at low conversions, it may be desirable to subject the product to one or more further treatments to further increase the content of aromatic hydrocarbons. In such cases it is usually desirable to separate high boiling polymers from the product between treatments.

The above examples, which have been presented solely to illustrate various aspects of the invention, are not to be considered as limiting the invention. It is to be understood that modifications will be readily 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 catalytic agent for the synthesis of aromatic hydrocarbons from open chain hydrocarbons consisting of compressed pills comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of from 90:10 to 50:40 respectively, and an alkali metal compound in an amount corresponding to from 2 to 50 atoms of alkali metal per each 100 molecules of said mixed oxides.

2. A process for converting open chain hydrocarbons to aromatic hydrocarbons which comprises contacting vapors of a hydrocarbon containing not more than 12 carbon atoms in an open chain and structurally capable of being cyclized to a six-membered ring at a temperature of from 400°C. to 600°C. and for a contact time of at least a 1/2 second with a catalyst comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of 90:10 to 60:40 respectively, and an alkali metal compound in an amount corresponding to from 15 to 20 alkali metal atoms per each 100 molecules of said mixed oxides, and periodically restoring the activity of said catalyst by treating with steam at a temperature of from 450°C. to 850°C.

A 3. A process for converting open chain hydrocarbons to aromatic hydrocarbons which comprises contacting vapors of a hydrocarbon containing not more than 12 carbon atoms in an open chain and structurally capable of being cyclized to a six-membered ring at a temperature of from 400°C. to 600°C. and for a contact time of at least a 1/2 second with a catalyst comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of 90:10 to 60:40 respectively, and an alkali metal compound in an amount corresponding to from 2 to 50 alkali metal atoms per each 100 molecules of said mixed oxides, and periodically restoring the activity of said catalyst by treating with steam at a temperature of from 450°C. to 850°C.

4. A process for the production of aromatic hydrocarbons which comprises contacting vapors of a hydrocarbon containing not more than 12 carbon atoms in an open chain and structurally capable of being cyclized to a six-membered ring at a temperature of from 400°C. to 600°C. and for a contact time of at least a 1/2 second with a catalyst comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of 90:10 to 60:40 respectively, and an alkali metal compound in an amount corresponding to from 15 to 20 alkali metal atoms per each 100 molecules of said mixed oxides.

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5. A process for the production of aromatic hydrocarbons which comprises contacting vapors of a hydrocarbon containing not more than 12 carbon atoms in an open chain and structurally capable of being cyclized into a six-membered ring at a temperature of from 400°C. to 600°C. with a catalyst comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of 90:10 to 60:40 respectively, and an alkali metal compound in an amount corresponding to from 2 to 50 alkali metal atoms per each 100 molecules of said mixed oxides.

6. A catalytic agent capable of catalyzing the synthesis of aromatic hydrocarbons from open chain hydrocarbons comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of from 90:10 to 60:40 respectively and potassium nitrate in an amount corresponding to from 15 to 20 atoms of potassium per each 100 molecules of said mixed oxides.

7. A catalytic agent capable of catalyzing the synthesis of aromatic hydrocarbons from open chain hydrocarbons comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of from 90:10 to 60:40 respectively and potassium hydroxide in an amount corresponding to from 15 to 20 atoms of potassium per each 100 molecules of said mixed oxides.

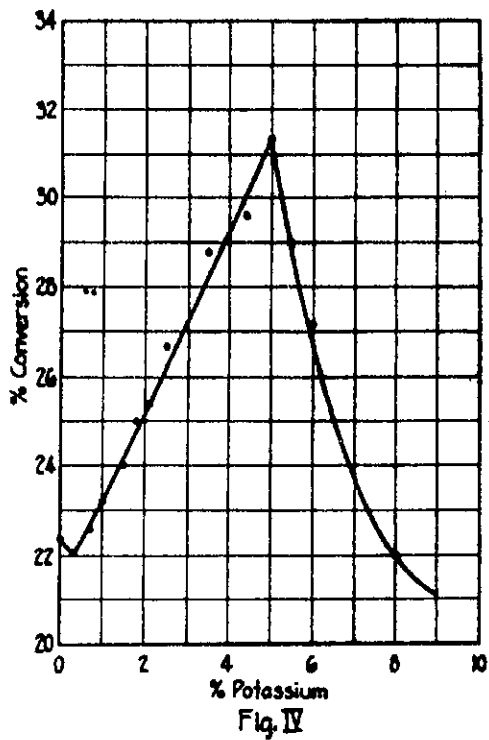
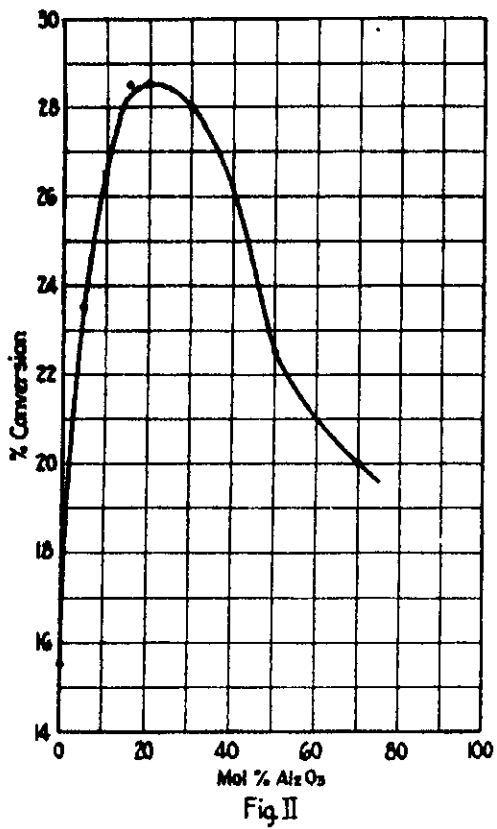
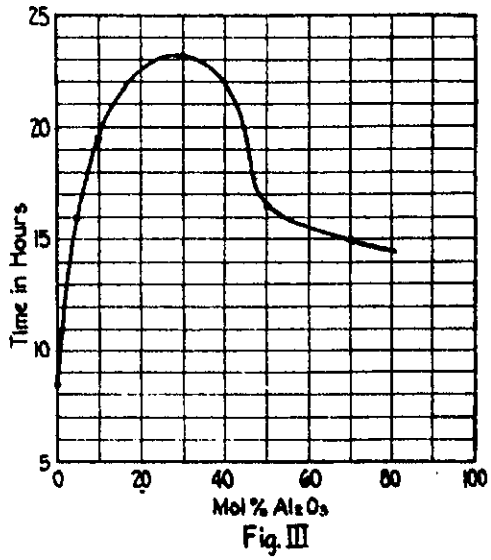
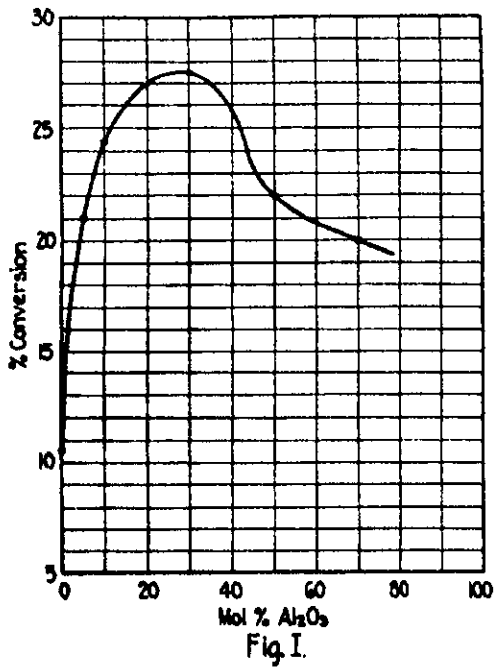
A

8. A catalytic agent capable of catalyzing the synthesis of aromatic hydrocarbons from open chain hydrocarbons comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of from 90:10 to 60:40 respectively and a potassium compound in an amount corresponding to from 15 to 20 atoms of potassium per each 100 molecules of said mixed oxides.

9. A catalytic agent capable of catalyzing the synthesis of aromatic hydrocarbons from open chain hydrocarbons comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of from 90:10 to 60:40 respectively and an alkali metal compound in an amount corresponding to from 15 to 20 atoms of alkali metal per each 100 molecules of said mixed oxides.

V

10. A catalytic agent capable of catalyzing the synthesis of aromatic hydrocarbons from open chain hydrocarbons comprising an intimate mixture of oxides of chromium and aluminum in a molecular ratio of from 90:10 to 60:40 respectively and an alkali metal compound in an amount corresponding to from 2 to 50 atoms of alkali metal per each 100 molecules of said mixed oxides.



Certified to be the drawings referred to
in the specification hereunto annexed.

Amsterdam, 16th August 1939

Gerardus Hendrikus Fisser.
Willem Frederik Engel
INVENTOR