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CYCLIZATION OF HYDROCARBONS

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The present invention relates to the cyclization of open chain hydrocarbons into closed chain or cyclic hydrocarbons. More particularly, the invention relates to an improved process involving the use of special catalysts whereby open chain hydrocarbons may be efficiently converted into aromatic hydrocarbons.

Aromatic hydrocarbons, as is known, find a very wide application and are of tremendous importance. Virtually the only source of these hydrocarbons is, however, as by-products from the distillation of coal. Consequently, their supply is primarily dependent upon the condition of the steel and coal tar industries and is in any case limited. Aside from the myriad of uses where their application is more or less obligatory, aromatic hydrocarbons have a great many potential uses which have been hitherto curtailed by the limited supply and relatively high prices. For example, aromatic hydrocarbons of relatively low molecular weight have become of increasing importance for use as solvents, etc. and especially as components of liquid fuels in view of their excellent ignition characteristics. In view of these circumstances there is an urgent demand for a practical and economical process whereby aromatic hydrocarbons may be produced from other sources.

The most promising source of aromatic hydrocarbons, other than coal tar, is petroleum. Aromatic hydrocarbons can be produced from petroleum hydrocarbons, at least theoretically, in any one of several ways, all of which have been studied in considerable detail. It is known, for example, that aromatic hydrocarbons are produced from non-aromatic petroleum hydrocarbons under severe thermal cracking conditions. Thus, cracked distillates obtained from high temperature or more or less severe cracking operations generally contain a certain amount of aromatic hydrocarbons. This method is, however, generally impractical for the production of pure aromatic hydrocarbons or highly aromatic hydrocarbon fractions in view of the low yields, excessive production of gas and extensive treatment required to separate the aromatic hydrocarbons formed from olefines, diolefines and other cracked products which are simultaneously formed.

It is also known that aromatic hydrocarbons may be produced by the thermal treatment of light hydrocarbon gases at high temperatures according to the Fischer process. This process, however, requires temperatures in the neighborhood of 1000° C. to 1300° C. and requires the use of a large number of expensive alloy reaction tubes of extremely small dimensions. The process furthermore tends to give relatively low yields of aromatic hydrocarbons which are predominantly of the less desired polynuclear type.

It has been found that aromatic hydrocarbons may be synthesized by the catalytic cyclization-dehydrogenation of open chain hydrocarbons. This new reaction holds considerable promise in that it allows aromatic hydrocarbons to be produced in almost any desired quantities from inexpensive and readily available hydrocarbons and particularly the normal aliphatic hydrocarbons which, in view of their poor ignition characteristics, are least desirable for gasoline-type fuels. A further advantage which can be gained by the utilization of catalytic cyclization is that, if naphthenic hydrocarbons are present in the hydrocarbon fraction treated, these may be simultaneously dehydrogenated to aromatic hydrocarbons, thus increasing the yield. In view of the great possibilities afforded by the cyclization reaction, a great deal of work has been done to bring this reaction into the realm of practical application.

The production of aromatic hydrocarbons by cyclization requires catalysts having dehydrogenating activity. This has been considered by some to indicate that the conversion of open chain hydrocarbons to aromatic hydrocarbons is a multi-step reaction involving dehydrogenation. It is therefore sometimes referred to as "cyclization-dehydrogenation," "dehydrogenation-cyclization" and "dehydrocyclization." It is known, however, that the cyclization ability of a given catalyst involves more than simply its dehydrogenating ability. Although nearly all classes of dehydrogenating catalysts have been investigated with regard to their possible cyclization activities, only a relatively few have been found to exert an appreciable cyclization activity. Cyclization activity appears to be practically confined to compounds of metals of the left-hand columns of groups IV, V and VI of the periodic table.

Of these, those of group VI and especially chromium are by far the most active.

The cyclization ability of the various catalytic metal compounds is, in general, relatively little affected by the type of compound in which the metal is combined. Thus, for example, the oxides, sulfides, halides, selenides, tellurides, phosphates, manganates, molybdates, chromates, chromites, tungstates, etc. or mixtures thereof may generally be employed. Generally speaking, however, the various cyclizing metals are preferably used in the form of their oxides.

These cyclizing metal compounds per se are, however, not generally suited for practical application due to the fact that they quickly lose their cyclizing activity in use. In order to produce aromatic hydrocarbons in a more economical manner, special combination catalysts having greater stability are invariably employed.

These cyclizing metal compounds are usually supported upon suitable carrier materials. Although most of the large variety of common catalyst carriers may be employed, a very beneficial stabilizing effect is obtained with carriers having appreciable adsorptive properties. Thus, for example, it is generally preferable to employ one of the so-called "activated" carriers such as activated carbon, activated coal, silica gel and the like. Especially suitable carriers are those comprising activated or adsorptive aluminas such, for instance, as the various activated alumina gels, activated bauxite and the like. A particularly effective adsorptive alumina is that prepared according to the process of U. S. Patent 1,868,869 and commonly used in the trade under the name "activated alumina."

The cyclizing metal compound and relatively inactive stabilizing compound may be employed in a wide range of proportions. In general, however, the stabilizing material functions also as a carrier material and is used in excess. Suitable catalysts may comprise, for example, an adsorptive and stabilizing carrier material supporting from 2% to 30% of a catalytically active metal in the form of a suitable compound such as an oxide, sulfide, or the like.

These supported catalysts may be prepared in any one of several conventional manners. A convenient method comprises impregnating a suitable carrier in the form of granules or pellets of the desired size with a solution of a compound of the metal which it is desired to combine with the carrier, and then drying. The concentration of the impregnating solution used in this particular case will depend upon the solubility of the particular metal compound at the temperature of the impregnation and upon the desired concentration of the metal compound in the compound catalyst. The procedure followed in drying or treating the impregnating material will vary depending upon the chemical constitution of the compound catalyst. In general, the material can be dried in air at temperatures as high as 800° C. or even higher in some cases. In other cases, it may be desirable to effect the drying with inert gases such as nitrogen, or reducing gases such as hydrogen, hydrocarbons, etc.

Many of the compounds which are desired as active cyclizing constituents of the combined catalyst, such as the oxides and sulfides, are not sufficiently water-soluble to permit direct impregnation of the carrier with their aqueous solutions. In such cases, the stabilizing carrier may be impregnated with a solution of a salt which can be converted to the desired metal oxide, metal sulfide or the like by calcination, hydrogen sulfide treatment, or the like, of the impregnated material. A cyclizing metal oxide-containing catalyst may also be obtained by precipitating a corresponding metal hydroxide on the surface of the carrier and subjecting the thus-obtained material to calcination under suitable temperature conditions.

The catalysts prepared as described are often submitted to a pretreatment prior to their use. Thus, for example, they are often heated for some hours at temperatures between about 300° C. and 600° C. in the presence of reducing gases such as hydrogen, hydrogen sulfide, hydrogen plus natural gas, etc. Such pretreatment usually improves their activity somewhat.

The process of cyclization-dehydrogenation to produce aromatic hydrocarbons using cyclizing metal compound catalysts is 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, it 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 I

Open chain hydrocarbon employed	Predominant aromatic hydrocarbons found in the reaction product
N-hexane	Benzene.
N-heptane	Toluene.
2-methyl hexane	Do.
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	Do.
N-octane	Ortho xylene.

The process is also applicable for the production of poly-nuclear hydrocarbons from alkylated cyclic hydrocarbons, such as n-butyl benzene, n-amyl benzene, n-butyl cyclohexane, crotyl benzene, and the like. Of the various applicable hydrocarbons, so that better results are, in general, obtained with normal and slightly branched hydrocarbons. Applicable hydrocarbon mixtures may also contain higher and/or lower boiling cyclizable and non-cyclizable hydrocarbons such as naphthenic hydrocarbons, paraffinic hydrocarbons, olefinic hydrocarbons, and the like. Thus, for example, normal heptane may be cyclized in the presence of methane, ethane, ethylene, benzene, toluene, octane, 2-methyl pentane, and the like, and excellent yields of toluene obtained. I have found, however, that materially improved catalyst life and therefore operating economy can be realized when treating hydrocarbon mixtures containing lower boiling non-aromatizable hydrocarbons, if such mixtures are first treated to remove the easily dehydrogenated and non-aromatizable butanes and pentanes. Isopentane, when present in substantial concentrations in the hydrocarbon

mixture, is particularly detrimental and is preferably removed.

The process is also 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, 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 anti-knock properties is obtained. The hydrocarbon treated is preferably substantially free of water and/or compounds, such as the alcohols which form water under the reaction conditions.

The hydrocarbon or hydrocarbon mixture to be treated 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 above atmospheric pressure (for instance, 0.01 to 50 atm.) are applicable, the process is usually executed in practice at atmospheric pressures or thereabouts, for instance, 1 to 10 atm.

In order to produce the best yields of aromatic hydrocarbons and realize the maximum efficiency of the catalyst, the cyclization is usually effected at a temperature between about 350° C. and 700° 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 usually lead to cracking and carbon deposition.

The contact time required to effect the formation of aromatic hydrocarbons by catalytic cyclization-dehydrogenation of open chain hydrocarbons is usually considerably longer than that required for dehydrogenation and usually is at least five seconds. Suitable contact times for operation in the above temperature range are, for instance, between about six seconds and two minutes. When operating within a preferred temperature range of about 450° C. to 550° C., optimum results are usually obtained with contact times between about six and eighty seconds.

The catalytic reaction is often executed in the presence of added hydrogen. The ratio of hydrogen to hydrocarbon may range, for example, from 0 up to about 5 mols per mol. The presence of hydrogen, it is found, tends to prolong the life of the catalyst by inhibiting side reactions which lead to tar and carbon formation. The use of added hydrogen is consequently of most advantage when treating complex hydrocarbon mixtures such as cracked gasoline stocks, etc. which ordinarily tend to tar and coke up the catalyst relatively quickly. The cyclization reaction is, however, inhibited by excessive hydrogen pressures. When hydrogen is used, its partial pressure is therefore preferably kept below about 10 atmospheres.

The state of the art relative to the cyclization of open chain hydrocarbons to aromatic hydrocarbons is illustrated by U. S. reissue Patents: 21,486, 21,588 and 21,464–7 inclusive.

The foregoing brief review of the art of synthesizing aromatic hydrocarbons from open chain hydrocarbons by catalytic cyclization-dehydrogenation is given to furnish a general background for indicating the improvement in this specific process embodied in the present invention.

The object of the present invention is to provide a method whereby aromatic hydrocarbons may be produced from open chain hydrocarbons through catalytic cyclization-dehydrogenation in a more advantageous manner, more particularly by providing a method which is particularly designed to take advantage of short cycle operation and which gives increased conversions. Specific objects of the invention are to provide an improved method for the production of aromatic hydrocarbons from single open chain hydrocarbons and simple mixtures thereof and to provide a more efficient method for the improvement of gasoline stocks, blending stocks and other hydrocarbon fractions through the catalytic conversion of relatively less desirable open chain hydrocarbons therein to valuable aromatic hydrocarbons.

Through a lengthy investigation of catalysts with respect to their cyclization activity, it has been found that the above-described method for the catalytic cyclization of open chain hydrocarbons to aromatic hydrocarbons may be considerably improved by employing, in lieu of the conventional catalysts, catalysts which are specifically promoted for the cyclization reaction by the incorporation therein of relatively small amounts of certain promoter metals. It has been found that when certain small amounts of platinum and/or palladium are incorporated in these conventional cyclization catalysts, as hereinafter more fully described, their cyclization activity is markedly promoted and that when such promoted catalysts are employed in otherwise conventional cyclization processes, greatly improved yields may be obtained. The more or less specific promoting effect of platinum and palladium on the cyclization activity of these catalysts is contrary to expectations since these metals per se are relatively poor cyclization catalysts. It has been shown, for instance [J. Gen. Chem. (U. S. S. R.) 9, 496 (1939)] that with a platinum catalyst the conversions of paraffin hydrocarbons to aromatic hydrocarbons are only in the range of 1% to 6%. Furthermore, the amounts of platinum and/or palladium required as promoters are quite small and far less than needed for even a poor cyclization. Furthermore, this promoting effect is practically confined to these metals. Other metals of group VIII of the periodic system are not equivalent. Of the materials which have been found to act as specific promoters for cyclization, namely, platinum and/or palladium, platinum is preferred.

The quantity of promoter metal or mixture of promoter metals incorporated in the cyclization catalyst in order to exhibit the desired promoter effect depends upon the amount of the metal as cyclizing metal compound in the catalyst. In general, the promoter metal is preferably present in an amount ranging from about 0.2% to about 2% of the metal in this cyclizing metal compound.

The promoter element is preferably incorporated into the cyclization catalyst by direct impregnation, as in the preparation of other conventional catalysts containing these metals. In promoting a cyclization catalyst with platinum, for instance, it may be impregnated with a suitable solution of platinum chloride. Other soluble salts of platinum and/or palladium may also be employed. Thus, for example, in the case of platinum one may impregnate the cyclization catalyst with suitable solutions of salts such as ammonium platinum chloride, alkali platinum chloride, barium platinum cyanide, etc. The im-

pregnated solutions may be prepared with either water or alcohol, or mixtures thereof. In impregnating the cyclization catalyst with such solutions of promoter salts, it is preferable to employ solutions of such concentrations that the entire impregnating solution is taken up by the catalyst. In this way catalysts having uniform and predetermined compositions may be most easily prepared without loss of valuable promoter salts, displacement, or the like.

The catalyst impregnated with the solution of the promoter substance may be treated in the manners conventional in making platinum or palladium catalysts to convert the impregnated promoter compound to the metal. Thus, for example, the impregnated catalyst may be dried at 50° C.–150° C. and finally heated to, for instance, 450° C. The catalyst may then, if desired, be pretreated with a reducing gas as described above.

The platinum and/or palladium promoters employed in these catalysts, it is found, act altogether differently than when employed as catalysts per se. For instance, it is known that platinum and palladium are notoriously susceptible to poisoning by sulfur and similar catalyst poisons. When employed as promoters for cyclizing metal compounds in the cyclization of open chain hydrocarbons, however, it is found that such catalyst poisons have no apparent adverse effect. Thus, for example, a catalyst promoted by platinum can be used in the cyclization of open chain hydrocarbons with sulfur as mercaptan or hydrogen sulfide actually added to the feed without impairing the cyclizing activity. It is found, however, that the activity of the cyclizing catalysts is adversely affected by sulfates in the catalyst mass. When promoting cyclizing catalysts with platinum or palladium, therefore, it is preferable that soluble sulfates, if these are present in appreciable concentrations, be first removed. Also, the impregnating solutions are preferably substantially sulfate-free. Thus, for example, when impregnating a suitable carrier with chromium oxide, superior results may be obtained by employing chromic acid or chromium nitrate which has been purified to remove sulfate impurities. Alkali metal compounds (except the sulfates), on the other hand, are not usually detrimental. In fact, it is found that small amounts of potassium or potassium compounds (other than the sulfate) are beneficial and that catalysts containing potassium (preferably 5% to 15% of the amount of metal in the cyclizing metal compound) along with the platinum and/or palladium are somewhat superior. Sodium, when present in appreciable concentrations, is known to exert a poisoning action on cyclizing catalysts. In small amounts, however, its presence may be ignored.

While the property of platinum and palladium to selectively promote cyclization appears to be general to all cyclizing metal compounds it is not equivalent in all catalysts. It appears to depend somewhat both upon the specific cyclizing metal compound promoted and upon the carrier material employed. In general, the promoter effect is most pronounced with metal compounds having the strongest cyclizing activity. Thus, the platinum and/or palladium promoters may be most advantageously employed with a supported chromium oxide catalyst. The reason for the difference in promoting action caused by the carrier material is not understood. It is, however, very clearly evident. It is found that the promoter effect is more pronounced when the promoter is applied to a cyclizing metal compound supported upon an alumina carrier than when it is supported upon other conventional carriers. Furthermore, all alumina carriers are not equivalent. It is found that the promoting effect of platinum and/or palladium is much more pronounced when the alumina carrier material consists essentially of or contains appreciable quantities of alumina alpha monohydrate. Such a material is "Activated Alumina." "Activated Alumina" is a particular form or kind of alumina prepared from the scaly deposits formed in the Fickes-Sherwin modification of the Bayer process, according to the process described in U. S. Patent 1,868,869.

The cyclization-dehydrogenation of open chain hydrocarbons using catalysts promoted with platinum and/or palladium, according to the process of the present invention, is illustrated in the following examples. These examples, which are in the nature of selected carefully executed comparable experiments carried out under favorable conditions with a few typical catalysts and with a simple representative hydrocarbon rather than illustrations of suitable applications of the process with a wide variety of catalysts and hydrocarbon stocks, were chosen for the purpose of illustrating and emphasizing various aspects of the promoting effect discussed above and should not be considered as limiting the invention in any way.

Example I

Excellent cyclization catalysts of the conventional type having the following compositions

Catalyst No.	Support	Cr (as chromium oxide)	Zn (as zinc oxide)
		Per cent	*Per cent*
183	"Activated alumina"	12.2	0.10
184	do	11.2	0.28
185	do	12.7	0.69

were employed under the following nearly optimum conditions

Temperature=490° C.
Pressure=1 atmosphere
Liquid hourly
space velocity=0.33

for the cyclization-dehydrogenation of pure normal heptane to toluene. The conversions to toluene obtained initially, at the maximum, and after five hours of operation are given in the following table:

Time	Conversions		
	Catalyst 183	Catalyst 184	Catalyst 185
	Per cent	*Per cent*	*Per cent*
Initial	24	33	13
Maximum conversion	49	49	49
Five hours	47	47	45

From the results of these experiments it is seen that catalyst 184 is the best, being slightly better than catalysts 183 or 185. These examples illustrate the results obtainable under favorable conditions with catalysts of the conventional type.

Example II

A quantity of catalyst having the same composition as catalyst 184 described above was im-

pregnated with 0.17% platinum (catalyst 176). This platinum-promoted catalyst was applied for the cyclization-dehydrogenation of normal heptane under the same conditions as those of Example I. The conversions to toluene obtained were as follows (the results obtained with catalyst 184 are included for comparison):

Time	Conversions	
	Catalyst 176	Catalyst 184
	Per cent	*Per cent*
Initial	84	33
Maximum conversion	84	49
Five hours	50	47

From this example it is seen that by promoting a conventional cyclization-dehydrogenation catalyst with a small amount of platinum, much better yields of aromatics may be obtained.

Example III

An excellent cyclization-dehydrogenation catalyst (No. 57) of the conventional type prepared by impregnating an adsorptive alumina with 10.5% chromium (as chromium oxide) was used in the cyclization-dehydrogenation of pure normal heptane under the following nearly optimum conditions:

Temperature=490° C.
Pressure=10 atmospheres
Diluent=Hydrogen, 1 mol/3 mols heptane
Contact time=70 seconds

The following results were obtained:

Average conversion to toluene over the first ten hours=7%
Bromine number of the product=11

When the hydrogen diluent was replaced with nitrogen in a comparable experiment, the following results were obtained:

Average conversion to toluene over the first ten hours=12%
Bromine number of the product=14

These experiments illustrate the results obtainable under favorable conditions with one of the best prior art cyclization catalysts for medium time cycle operation. The distinct retardation of the cyclization reaction caused by the 2½ atmospheres partial pressure of hydrogen is readily apparent.

Example IV

A catalyst similar to the above-described catalyst 57 (containing 13.8% chromium as chromium oxide) was impregnated with 0.087% of platinum (catalyst 232). This promoted catalyst was employed for the cyclization of normal heptane under the same conditions as shown in Example III. The results obtained were as follows:

Average conversion to toluene over the first ten hours=17%
Bromine number=9

When the hydrogen diluent was replaced by an equal amount of nitrogen, the results obtained were as follows:

Average conversion to toluene over the first ten hours=21%
Bromine number=15

It is seen that, by comparing Examples III and IV, the promotion of the catalyst with as little as 0.087% platinum about doubled the conversions to toluene obtained in a process period of ten hours. It is also seen that, although the conversions obtained in both cases with the promoted catalyst were much higher than those obtained with the unpromoted catalyst, the bromine numbers of the products were lower. This is unexpected and is due to the fact that the platinum promoter is quite specific and is primarily effective in increasing the cyclization activity of the catalyst.

Example V

Several comparable chromium oxide-alumina cyclization catalysts were prepared and some were promoted for cyclization with small amounts of platinum. Their active component compositions were as follows:

Catalyst No.	Chromium oxide	Zinc oxide	Platinum
57	10.5% Cr	0	0.
234	13.0% Cr	0	0.085% Pt.
184	11.2% Cr	0.28% Zn	0.
233	13.8% Cr	0.39% Zn	0.042% Pt.
232	13.8% Cr	0.39% Zn	0.087% Pt.
176	11.4% Cr	0.29% Zn	0.17% Pt.

These catalysts were used for the cyclization-dehydrogenation of normal heptane under the following conditions:

Temperature=490° C.
Pressure=1 atmosphere
Liquid hourly space velocity=0.33

The initial conversions, maximum conversions, and average conversions over the first 7½, 10, and 25 hours are given in the following table:

Catalyst No.	Initial conversion	Maximum conversion	Average conversion over		
			7½ hrs.	10 hrs.	25 hrs.
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
57	13	44	41.7	40	31
234	80+	80+	50.6	46.9	33.4
184	33	49	43	42	34
233	70	70	43.5	39.8	27.0
232	79	79	54	48	34
176	84	84	57	52	36

From these results it is seen that, although concentrations of platinum promoter as small as 0.3% of the chromium concentration in the catalyst (catalyst 233) are effective in materially increasing the initial conversion, such amounts do not produce the optimum promotion even for fairly short cycle operation (compare, for example, the average conversions over the first 7½ hours). A concentration of platinum of about 0.63% of the chromium concentration (catalyst 232) gives much greater conversions in short cycle operation, is approximately 125% efficient in 7½-hour cycles, and is even definitely superior in 10-hour cycles. Over about 25 hours the average conversions are about equal. Catalyst 176 containing about 1.5% platinum (based on the amount of chromium in the chromium oxide) gives much superior conversions in short cycle operation, 7½-hour cycle operation and 10-hour cycle operation, and even the average conversions obtained in 25-hour cycle operation are improved. Example V therefore clearly illustrates the effect of the concentration of promoter and the advantageous results made possible by the present method, especially when using short cycle operation.

Example VI

A conventional chromium oxide-alumina cyclization catalyst containing 10.5% chromium was promoted by the addition of 0.08% palladium (catalyst 267). This catalyst was used for the cyclization of pure normal heptane under the following nearly optimum conditions:

Temperature=490° C.
Pressure=1 atmosphere
Liquid hourly space velocity=0.33

Conversions to toluene obtained initially, at the maximum and the average obtained over the first 7½, 10 and 25 hours of operation are given in the following table. The results obtained with a comparable catalyst to which no palladium promoter was added are given for comparison.

Conversion to toluene	Non-promoted catalyst	Palladium-promoted catalyst
	Per cent	*Per cent*
Initial	13	66
Maximum	44	66
7½ hours average	41.7	49.1
10 hours average	40	46.4
25 hours average	31.1	33.5

It is seen from these results that palladium is essentially as effective a promoter for cyclization-dehydrogenation as platinum. The initial conversions obtained with palladium-promoted catalysts are slightly lower, but the averages in medium cycle operation are equal to, if not slightly better than, those obtained with platinum-promoted catalysts. Other elements of Group VIII are not equivalent to platinum and/or palladium in their promoting effect. Cobalt, for instance, when applied to the above catalyst 57 (0.08%) under conditions comparable with those of Example VI affords average conversions of only 41.7%, 39.8% and 30.4% for the first 7½, 10 and 25 hours, respectively. Nickel and ruthenium act similarly.

Example VII

Two comparable experiments were made using the above-described catalyst 234 (containing 0.085% Pt) in which the normal heptane feed was altered by the addition of 0.05% and 0.25%, respectively, of sulfur in the form of diethyl sulfide. The deviations of the conversion curves for both of the experiments from those obtained with pure normal heptane feed with the same catalyst were within the limits of error of the measurements. The experiment with the heptane having the higher sulfur content, in fact, gave slightly better conversions than were obtained with the sulfur-free feed.

The advantage of the present process over the prior art process such as described above is that, due to the specific promoting effect of the specified quantities of platinum and/or palladium on cyclizing metal compound catalysts, greatly improved conversions may be obtained. As is illustrated in the above examples, the improved conversions are particularly pronounced in the initial operating stages, i. e. during the first few hours of processing after each regeneration. The present process is therefore especially advantageous in that it allows the cyclization to be effected with much higher conversions with short cycle operation. The exceptional advantage of the present process in short cycle operation will be more clearly evident from the following considerations:

(1) In catalytic cyclization it is a general rule that catalysts which show the highest cyclization activity decline in activity faster than those having lower activities. This refers to the temporary loss of activity which is caused by the deposition on the catalyst of small amounts of carbonaceous deposits and is probably due to the fact that the amount of carbonaceous deposits formed is more or less proportional to the amount of reaction catalyzed. As a result, in the initial stages of operation, i. e. in the first 2–10 hours after any regeneration, the superiority of the promoted catalyst over the non-promoted catalyst is greater than after long periods of operation.

(2) Cyclization catalysts do not, in general, exhibit their maximum activity immediately upon being put on-stream but require a certain induction period (generally in the order of 1–6 hours), during which lower than optimum conversions are obtained. The promoted catalysts used in the process of the present invention, on the other hand, afford maximum conversions almost immediately upon being put on-stream, i. e. in the process of the present invention the induction period is substantially absent. As a result of these two factors the initial conversions to aromatic hydrocarbons obtainable in the present process are often several times as high as those obtained by prior art methods, and conversions over short cycle periods are much superior. The average conversions over long cycle periods, although superior to those using prior art cyclization catalysts, are not superior in the outstanding degree that they are in short cycle operation.

I claim as my invention:

1. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of from about 2% to 30% of chromium as chromium oxide supported upon an adsorptive alumina and promoted with from about 0.02% to 0.5% of platinum.

2. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing oxide of a metal selected from the left-hand column of group VI of the periodic table supported upon a major proportion of a stabilizing carrier consisting essentially of alumina alpha monohydrate and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

3. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing oxide of a metal selected from the left-hand column of group VI of the periodic table supported upon a major proportion of an adsorptive alumina and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

4. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises

contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of from about 2% to 30% chromium as chromium oxide supported upon a stabilizing carrier of relatively low catalytic activity and promoted with about .07% to .2% of platinum.

5. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing compound of chromium supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with from about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of platinum.

6. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing compound of a metal selected from the left-hand column of group VI of the periodic table supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with from about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of platinum.

7. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of chromium oxide supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

8. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing oxide of a metal selected from the left-hand column of group VI of the periodic table supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

9. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing oxide of a metal selected from the left-hand columns of groups IV, V and VI of the periodic table supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

10. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing compound of chromium supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

11. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing compound of a metal selected from the left-hand column of group VI of the periodic table supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

12. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from six to twelve carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing compound of a metal selected from the left-hand columns of groups IV, V and VI of the periodic table supported upon a major proportion of a stabilizing carrier of relatively low catalytic activity and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

13. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from 6 to 12 carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing compound of a metal selected from the left-hand columns of groups IV, V and VI of the periodic table supported upon a major proportion of a stabilizing carrier consisting essentially of alumina alpha monohydrate and promoted with about 0.2% to 2% based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

14. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from 6 to 12 carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing oxide of a metal selected from the left-hand columns of groups IV, V and VI of the periodic table supported upon a major proportion of a stabilizing carrier consisting essentially of alumina alpha monohydrate and promoted with about 0.2% to 2% (based on the amount of metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

15. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from 6 to 12 carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of a cyclizing compound of chromium supported upon a major proportion of a stabilizing carrier consisting essentially of alumina alpha monohydrate and promoted with about 0.2% to 2% (based on the amount of

metal in the cyclizing compound) of a metal selected from the group consisting of platinum and palladium.

16. Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons having from 6 to 12 carbon atoms which comprises contacting the aliphatic hydrocarbon under cyclizing conditions with a solid compound catalyst consisting essentially of chromium oxide supported upon a major proportion of a stabilizing carrier consisting essentially of alumina alpha monohydrate and promoted with about 0.2% to 2% (based on the amount of chromium) of a metal selected from the group consisting of platinum and palladium.

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