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TREATMENT OF HYDROCARBONS

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This invention relates particularly to the conversion of straight chain hydrocarbons into closed chain or cyclic hydrocarbons.

More specifically it is concerned with a process involving the use of particular catalysts and specific conditions of operation in regard to temperature, pressure, and time of reaction whereby aliphatic hydrocarbons can be converted efficiently into aromatic hydrocarbons.

In the straight pyrolysis of pure hydrocarbons or hydrocarbon mixtures, such as those encountered in fractions from petroleum or those occurring naturally or produced synthetically, the reactions involved which produce aromatics from paraffins and olefins are of a complicated character and are difficult to control.

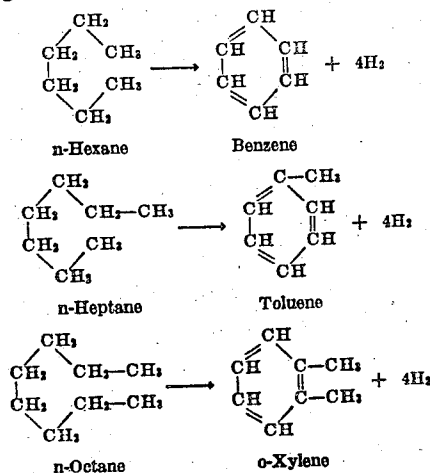
The search for catalysts to specifically control and accelerate desired conversion reactions among hydrocarbons has been attended with the usual difficulties encountered in finding catalysts for other types of reactions since there are no basic laws or rules for predicting the effectiveness of catalytic materials and the art as a whole is in a more or less empirical state. In using catalysts even in connection with conversion reactions among pure hydrocarbons and particularly in connection with the conversion of the relatively heavy distillates and residua which are available for cracking, there is a general tendency for the decomposition reactions to proceed at a very rapid rate, necessitating the use of extremely short time factors and very accurate control of temperature and pressure to avoid too extensive decomposition. There are further difficulties encountered in maintaining the efficiency of catalysts employed in pyrolysis since there is usually a rapid deposition of carbonaceous materials on their surfaces and in their pores.

The foregoing brief review of the art of hydrocarbon pyrolysis is given to furnish a general background for indicating the improvement in such processes which is embodied in the present invention, which may be applied to the treatment of pure paraffin or olefin hydrocarbons, hydrocarbon mixtures containing substantial percentages of paraffin hydrocarbons such as relatively close cut fractions producible by distilling petroleum, and analogous fractions which contain unsaturated as well as saturated straight chain hydrocarbons, such fractions resulting from cracking operations upon the heavier fractions of petroleum.

In one specific embodiment the present invention comprises a process for producing aromatic

hydrocarbons from aliphatic hydrocarbons including paraffins and olefins which comprises subjecting said aliphatic hydrocarbons at a temperature in the approximate range of 450–650° C. to contact for different times of the order of 0.1–60 seconds with a catalytic material comprising essentially a major proportion of thorium oxide and a relatively minor proportion of oxides of elements selected from the members of the left-hand columns of groups 5 and 6 of the periodic table.

According to the present invention aliphatic or straight chain hydrocarbons having 6 or more carbon atoms in chain arrangement in their structure are specifically dehydrogenated in such a way that the chain of carbon atoms undergoes ring closure with the production in the simplest case of benzene from n-hexane or n-hexene and in the case of higher molecular weight paraffins of various alkyl derivatives of benzene. Under properly controlled conditions of temperature, pressure, and time of contact, very high yields of the order of 75 to 90% of the benzene or aromatic compounds are obtainable which are far in excess of any previously obtained in the art either with or without catalysts. For the sake of illustrating and exemplifying the types of hydrocarbon conversion reactions which are specifically accelerated under the preferred conditions by the present types of catalysts, the following structural equations are introduced:



Ethyl benzene and m-xylene and p-xylene are also formed from n-octane by a combination of reactions involving dehydrogenation, cyclization, and isomerization, but no idea is offered as to

the probable order in which these reactions occur.

In the foregoing table the structural formula of each of the primary paraffin hydrocarbons has been represented as a nearly closed ring instead of by the usual linear arrangement for the sake of indicating the possible mechanisms involved. No attempt has been made to indicate the possible intermediate existence of mono-olefins, diolefins, hexamethylenes or alkylated hexamethylenes which might result from the loss of various amounts of hydrogen. It is not known at the present time whether ring closure occurs at the loss of one hydrogen molecule or whether dehydrogenation of the chain carbons occurs so that the first ring compound formed is an aromatic such as benzene or one of its derivatives. The above three equations are of a relatively simple character indicating generally the type of reactions involved but in the case of n-paraffins or mono-olefins of higher molecular weight than the octane shown and in the case of branch chain compounds which contain various alkyl substituent groups in different positions along the 6-carbon atom chain, more complicated reactions will be involved. For example, in the case of such a primary compound as 2,3-dimethyl hexane the principal resultant product is apparently o-xylene although there are concurrently produced definite yields of such compounds as ethyl benzene indicating an isomerization of two substituent methyl groups. In the case of nonanes which are represented by the compound 2,3,4-trimethyl hexane, there is formation not only of mesitylene but also of such compounds as methyl ethyl benzene and various propyl benzenes.

It will be seen from the foregoing that the scope of the present invention is preferably limited to the treatment of aliphatic hydrocarbons which contain at least 6 carbon atoms in straight chain arrangement. In the case of paraffin hydrocarbons containing less than 6-carbon atoms in linear arrangement, some formation of aromatics may take place due to primary isomerization reactions although obviously the extent of these will vary considerably with the type of compound and the conditions of operation. The process is readily applicable to paraffins from hexane up to dodecane and their corresponding olefins. With increase in molecular weight beyond this point the percentage of undesirable side reactions tends to increase and yields of the desired alkylated aromatics decrease in proportion.

The thorium oxide carrier referred to above has a relatively low dehydrogenating activity, while the oxides of the elements mentioned are of relatively high catalytic activity and furnish by far the greater proportion of the observed catalytic effects. The oxides of these several elements vary somewhat in catalytic activity in any given reaction comprised within the scope of the invention and this variation will be greater in the case of different types of dehydrogenation and isomerization reactions.

In regard to the preparation of thoria employed as a carrier or support for the preparation of dehydrocyclization catalyst, it may be stated that thoria may be obtained by known methods from a number of minerals including thorite, orangite, and thorianite.

The catalytic dehydrogenating efficiency of thorium is greatly improved by the presence of oxides of the preferred elements in relatively minor amounts. The oxides which constitute the principal active catalytic materials may be deposited upon the surface and in the pores of

the thoria granules by several alternative methods such as for example the ignition of nitrates which have been absorbed or deposited from aqueous solution by evaporating or by similar ignition of precipitated hydroxides. As an alternative method though obviously less preferable the finely divided oxides may be composited mechanically with the thoria granules either in the wet or in the dry condition. The point of achieving the most uniform practical distribution of the oxides on the thoria should be borne in mind constantly since the observed catalytic effects evidently depend principally on surface action.

The oxide of vanadium which results from ignition of the nitrate, the hydroxide, or the carbonate is principally the pentoxide V_2O_5 which is reduced by hydrogen to form the tetroxide V_2O_4 , or the corresponding dioxide VO_2 and then to the sesquioxide V_2O_3 . In any case the primary deposition of vanadium compounds upon thoria granules may be made by the use of the soluble vanadyl sulfate or the nitrate and also solutions of ammonium and alkali metal vanadates may be employed, which furnish alkaline residues on ignition. It is probable that the sesquioxide is the principal compound which accounts for the catalytic activity observed with vanadium catalysts in reactions of the present character.

Columbium has several oxides which may be employed as catalyst components supported by thoria although the lower oxides are most likely to exist under the conditions employed in the process. The pentoxide Cb_2O_5 results from the ignition of the pentahydroxide which may be precipitated from solutions of soluble compounds such as the mixed fluoride of columbium and potassium. Solutions of alkali metal columbates may also be employed as a source of catalytic material, these furnishing an alkaline residue on drying and ignition. The pentoxide is definitely reduced by hydrogen or by hydrocarbons at the preferred temperatures of operation so that the essential catalysts for the major proportion of a run will probably include the lower oxides Cb_2O_3 and CbO .

The element tantalum which has the highest atomic number of the fifth group of elements herein mentioned, also has the pentoxide Ta_2O_5 , a tetroxide Ta_2O_4 and probably a sesquioxide Ta_2O_3 . The higher oxide is prepared by the ignition of the precipitated pentahydroxide precipitated from soluble salts.

The element chromium has three oxides, the trioxide CrO_3 , the dioxide CrO_2 , and the sesquioxide Cr_2O_3 , the last named being readily produced by heating the trioxide in hydrogen or hydrocarbon vapors at a temperature of 250° C. The dioxide has been considered to be an equimolecular mixture of the trioxide and the sesquioxide. The oxides are readily developed on the surface and in the pores of thoria granules by utilizing primary solutions of chromic acid H_2CrO_4 or chromium nitrate $Cr(NO_3)_3$. The ignition of the chromic acid, the nitrate, or the precipitated trihydroxide produces primarily the trioxide which is then reduced to the sesquioxide to furnish an active catalyst for use in reactions of the present character.

The two most important oxides of molybdenum which are employed alternatively in the production of dehydrocyclization catalysts, according to the present invention, are the dioxide MoO_2 , and the sesquioxide Mo_2O_3 . Since the reduction of the trioxide by hydrogen begins at about 300° C. and the reduction is rapid at 450°

C. the effective catalytic material is principally the sesquioxide. The trioxide may be added to the active thorium carrier from a solution of ammonium molybdate which is added in amounts just requisite to wet the carrier granules uniformly and the mass is then dried and calcined.

The element tungsten has three oxides; the trioxide WO_3 , the dioxide WO_2 , and the sesquioxide W_2O_3 . The trioxide is readily soluble in aqueous ammonia from which it may be deposited upon thorium granules and it is ordinarily reduced preliminary to service by the action of hydrogen at a relatively high temperature. Tungstic acids may be precipitated from the hydrated oxides and these may be heated to drive off water and leave a residue of oxides on the carrier particles.

In regard to uranium, which is the heaviest member of the present natural group of elements whose oxides are preferred as catalysts, it may merely be stated that while this element furnishes catalytic oxides having some order of catalytic activity, its scarcity and cost naturally preclude its extensive use in practice.

It has been found essential in the production of high yields of aromatics from paraffinic hydrocarbons when using the preferred types of dehydrocyclization catalysts that, depending upon the paraffinic hydrocarbon or mixture of hydrocarbons being treated, temperatures from 450 to 650° C. should be employed, contact times of approximately 0.1-60 seconds, and pressures approximating atmospheric. The use of sub-atmospheric pressure of the order of $\frac{1}{4}$ atmosphere may be beneficial in that reduced pressure generally favors selective dehydrogenation reactions, but on the other hand moderately superatmospheric pressure, usually of the order of less than 100 pounds per square inch, increases the capacity of commercial plant equipment, so that in practice a balance is struck between these two factors.

While the present process is particularly applicable to the production of the corresponding aromatics from an aliphatic hydrocarbon or a mixture of aliphatic hydrocarbons the invention may be employed also to produce aromatics from olefinic hydrocarbon mixtures such as distillates from paraffinic or mixed-base crude petroleum. In this case the aromatic character of the distillate will be increased and as a rule the octane number of the product will be higher than that of the charging stock. If desired and found feasible on a basis of concentration, the aromatics produced in the hydrocarbon mixtures may be recovered as such by distillation to fractions of proper boiling range followed by chemical treatment with reagents capable of reacting selectively with them. Another method for concentrating aromatics will involve the use of selective solvents such as liquid sulfur dioxide, furfural, chloroform, and alcohols.

Thus by the process of this invention a paraffinic gasoline, naphtha, or other hydrocarbon fraction may be contacted with a thorium-containing dehydrocyclization catalyst so as to produce a 20-50% yield of aromatic hydrocarbons per pass admixed with relatively small proportions of similarly formed olefins and unconverted paraffins. For effecting this cyclization the paraffinic fraction is contacted, for example, with a material comprising granular activated thorium supporting 4-32% by weight of chromium sesquioxide. The cyclized material containing relatively small amounts of olefins may be recycled

to further contact with the dehydrocyclization catalyst so as to convert these olefins into further quantities of aromatics and form a substantially olefin-free aromatic product.

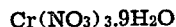
These catalysts consisting of thorium activated by oxides of the elements of the left-hand columns of groups 5 and 6 of the periodic table may be composited with stabilizing oxides such as magnesium oxide to produce a catalyst composite which retains its aromatic-forming activity after many periods of use and reactivation by burning off carbonaceous deposits in an oxygen-containing atmosphere. Composites of thorium and activating metal oxides such as are hereinabove described effect a relatively high conversion of paraffins into aromatics per pass together with high total liquid hydrocarbon recovery and relatively low gas formation.

The process of this invention makes possible the production of aromatic concentrates or aromatic-paraffinic hydrocarbon mixtures which are free from olefins and suitable for solvent extraction or other methods of separating pure aromatics, or which may be used directly for nitration or for other chemical reactions to which the presence of olefins would be objectionable. By this process the olefins formed incidental to the cyclization reaction are converted into aromatics thereby increasing further the yield of these desirable hydrocarbons.

The following example is introduced to show results obtainable in the operation of the process, although these data are not presented with the intention of unduly limiting the broad scope of the invention:

EXAMPLE

A catalyst containing 8% by weight of chromium sesquioxide and 92% by weight of thorium oxide was prepared by dissolving 84.2 parts by weight of crystalline chromic nitrate,



and 385 parts by weight of thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$, in 8000 parts by weight of water, followed by precipitating the hydrated oxides by addition of 225 parts by weight of concentrated ammonium hydroxide solution. The precipitates were removed from the solution by filtration, washed with distilled water, dried at 150-200° C., then pressed into cakes on a hydraulic press, and later broken and sized to produce 10-12 mesh particles which were calcined in a stream of dry air at 550° C. for one hour.

This granular calcined catalyst was employed as a filler in a tube through which normal heptane was passed at 550° C. at a charging rate corresponding to an hourly liquid space velocity of 2. Table 1 gives results obtained on normal heptane in the presence of the above described catalyst consisting of approximately 8% chromium sesquioxide and 92% thorium.

TABLE 1

Cyclization of normal heptane in the presence of 8% chromium sesquioxide and 92% thorium

Yields, weight per cent of charge:

Total hydrocarbon	93.2
Toluene	24.2
Carbon	1.9
Gas, uncondensed	6.8

Yields, weight per cent of heptane decomposed:

Toluene	78.2
Gas	21.9

Composition of hydrocarbon recovery, weight per cent:

Paraffins	62
Olefins	12
Naphthenes	0
Aromatics	26

Analysis of gas, vol. per cent:

Hydrogen	89.4
Olefins	1.4
Paraffins	8.9
Carbon index	1.53
Carbon monoxide	0.3

The results given in Table 1 show that a relatively high per cent of the heptane decomposed was converted into toluene in the presence of the chromium sesquioxide-thoria catalyst, the yields of toluene per pass being of the order of 26% by weight of the charge.

The foregoing specification and example show clearly the character of the invention and the results to be expected in its application to aliphatic hydrocarbons including paraffins and olefins, although neither section is intended to unduly limit its generally broad scope.

I claim as my invention:

1. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing at least six carbon atoms in straight chain arrangement which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons under dehydrocyclization conditions of temperature and pressure in the presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of an element selected from the members of the left-hand column of group 6 of the periodic table.

2. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing straight chains of 6-12 carbon atoms per molecule which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons under dehydrocyclization conditions of temperature and pressure in the presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of an element selected from the members of the left-hand column of group 6 of the periodic table.

3. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing straight chains of 6-12 carbon atoms per molecule which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons at a temperature of the order of 450-650° C. in the presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of an element selected from the members of the left-hand column of group 6 of the periodic table.

4. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing straight chains of 6-12 carbon atoms per molecule which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons at a temperature of the order of 450-650° C. under a pressure in the range of substantially atmospheric to approximately 100 pounds per square inch in the

presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of an element selected from the members of the left-hand column of group 6 of the periodic table.

5. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing straight chains of 6-12 carbon atoms per molecule which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons at a temperature of the order of 450-650° C. under a pressure in the range of substantially atmospheric to approximately 100 pounds per square inch for an average time of contact of approximately 0.1-60 seconds in the presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of an element selected from the members of the left-hand column of group 6 of the periodic table consisting of chromium, molybdenum, tungsten, and uranium.

6. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing straight chains of 6-12 carbon atoms per molecule which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons at a temperature of the order of 450-650° C. under a pressure in the range of substantially atmospheric to approximately 100 pounds per square inch for an average time of contact of approximately 0.1-60 seconds in the presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of chromium.

7. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing straight chains of 6-12 carbon atoms per molecule which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons at a temperature of the order of 450-650° C. under a pressure in the range of substantially atmospheric to approximately 100 pounds per square inch for an average time of contact of approximately 0.1-60 seconds in the presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of molybdenum.

8. A process for producing aromatic hydrocarbons from aliphatic hydrocarbons containing straight chains of 6-12 carbon atoms per molecule which comprises dehydrogenating and cyclizing said aliphatic hydrocarbons at a temperature of the order of 450-650° C. under a pressure in the range of substantially atmospheric to approximately 100 pounds per square inch for an average time of contact of approximately 0.1-60 seconds in the presence of a dehydrocyclization catalyst comprising essentially a major proportion of thorium oxide and relatively minor proportions of magnesium oxide and an oxide of an element selected from the members of the left-hand column of group 6 of the periodic table consisting of chromium, molybdenum, tungsten, and uranium.

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