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## TREATMENT OF CYCLIC HYDROCARBONS

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This invention relates particularly to the treatment of cyclic hydrocarbons which are characterized by partial or complete saturation of the ring and relates therefore to such hydrocarbons as cyclo-hexane and its alkylated derivatives, and also cyclo-hexene and cyclo-hexa-diene and their corresponding alkyl derivatives. While the process of the invention to be disclosed is more particularly applicable to the treatment of naphthene hydrocarbons of 6 carbon atoms in the ring, there will be some effect on the hydrocarbons of 5, 7, and higher carbon-atoms, particularly when these have a tendency to isomerize under the conditions of treatment, to the corresponding 6 carbon-atom ring compounds.

In one aspect of the invention it may be directed to the production of more highly unsaturated compounds from cyclo-hexane, cyclo-hexene, and cyclo-hexa-diene to the extent of producing benzol from these compounds or alkylated benzols from their alkyl derivatives and in another aspect, it is related to the treatment of mixtures of naphthenes such as those present in naphthenic gasolines or similar compounds present in cracked gasolines although there would generally be a relatively low percentage of the completely unsaturated ring compounds in cracked gasolines. The value of the process in the treatment of pure compounds is to produce more highly reactive hydrocarbons in the case of gasolines to produce compounds of higher antiknock value. The process to be disclosed may be operated so as to selectively effect dehydrogenation of ring hydrocarbons without essential change in structure or any undesirably large amounts of side reactions.

In one specific embodiment the present invention comprises the treatment of naphthenic hydrocarbons for the dehydrogenation thereof by subjecting said hydrocarbons at elevated temperatures and substantially atmospheric or subatmospheric pressures to contact with solid granular catalysts comprising major proportions by weight of carrying materials of relatively low catalytic activity supporting minor proportions by weight of compounds of the elements in the lefthand column of group V of the periodic table, and preferably the oxides thereof which have relatively high catalytic activity in furthering straight dehydrogenation reactions.

The present invention is characterized by the use of particular catalytic materials and suitable combinations of temperature, pressure, and time of contact to control the character and extent of the dehydrogenation of naphthenic hydrocarbons to produce high yields of desired products and a minimum of undesirable byproducts. Temperatures from approximately 400 to 650° C. may be employed, pressures from moderately superatmospheric of the order of 50 to 100 lbs. per square inch down to those of the order of 0.25 atmospheres absolute and times of contact from approximately 0.1 to 30 seconds. Obviously the interrelated conditions of temperature, pressure, catalyst activity, and time of contact will be varied with different compounds or mixtures of compounds undergoing treatment and with the extent of dehydrogenation desired. For example, to produce benzene from cyclo-hexane may require more severe conditions in these interrelated factors than in the production of benzene from cyclo-hexa-diene, which is already partly dehydrogenated. Variables will also be introduced when alkyl derivatives of the ring compounds are treated.

In the present instance, the catalysts which are preferred for selectively dehydrogenating naphthenic hydrocarbons have been evolved as the result of a large amount of investigation with catalysts having a dehydrogenating action upon various types of hydrocarbons, such as, for example, those which are encountered in the fractions produced in the distillation and/or pyrolysis of petroleum and other naturally occurring hydrocarbon oil mixtures. The criterion of an acceptable dehydrogenating catalyst is that it shall split off hydrogen without inducing either scission of the bonds between carbon atoms or carbon separation.

It should be emphasized that in the field of catalysts there have been very few rules evolved which would enable the prediction of what materials will catalyze a given reaction. Most of the catalytic work has been done on a purely empirical basis, though at times certain groups of elements or compounds have been found to be more or less equivalent in accelerating certain types of reactions. For example, the noble metals, platinum, and palladium, have been found to be effective in dehydrogenating reactions, particularly in dehydrogenating naphthenes to form aromatics, but these metals are expensive and easily poisoned by traces of sulfur so that their use is considerably limited in petroleum hydrocarbon reactions.

The present invention is characterized by the use of a particular group of composite catalytic materials which employ as their base catalysts or carriers certain refractory oxides and silicates which in themselves may have some slight spe-

cific catalytic ability in the dehydrogenating reactions but which are improved greatly in this respect by the addition of certain promoters or secondary catalysts in minor proportions, which comprise in the present instance the compounds and preferably the oxides of the element in the lefthand column of group V of the periodic table including vanadium, columbium, and tantalum. The base supporting materials for these compounds are preferably of a rugged and refractory character capable of withstanding the severe use to which the catalysts are put in regard to temperature during service and in regeneration by means of air or other oxidizing gas mixtures after they have become fouled with carbonaceous deposits after a period of service. As examples of materials which may be employed in granular form as supports for the preferred catalytic substances may be mentioned the following:

| | |
|---|---|
| Magnesium oxide | Kieselguhr |
| Aluminum oxide | Crushed silica |
| Bauxite | Crushed firebrick |
| Bentonite clays | Glauconite (greensand) |
| Montmorillonite clays | |

The active compounds or promoters which are used in the catalyst composites according to the concepts of the present invention constitute a natural group since they are the elements in the lefthand column of group V of the periodic table. While the compounds and particularly the oxides of these elements are effective catalysts in the dehydrogenation reactions, it is not intended to infer that the different compounds of any one element or the corresponding compounds of different elements are exact equivalents in their catalytic activity.

In general practically all of the compounds of the preferred elements will have some catalytic activity in dehydrogenating naphthenic hydrocarbons though as a rule the oxides and particularly the lower oxides are the best catalysts. Catalyst composites may be prepared by utilizing the soluble compounds of the elements in aqueous solutions from which they are absorbed by prepared granular carriers or from which they are deposited upon the carriers by evaporation of the solvent. The invention further comprises the use of catalyst composites made by mechanically mixing relatively insoluble compounds with carriers either in the wet or the dry condition. In the following paragraphs some of the compounds of the elements listed above are given which are soluble in water and which may be used to add catalytic material to carriers.

*Vanadium*

Catalysts comprising 2 to 20 per cent by weight of the lower oxides of vanadium such as the sesquioxide $V_2O_3$ and the tetroxide $V_2O_4$ may be used. Some of the monoxide VO may be present in some instances. The oxides mentioned are particularly efficient as catalysts for the present types of reactions but the invention is not limited to their use but may employ other compounds of vanadium. Thus solutions of the ammonium and the alkali metal vanadates may be employed to add vanadium compounds to the carriers and also the soluble vanadyl sulfates and the vanadium nitrate and carbonate. The alkaline earth vanadates may be mixed mechanically and also the halides of vanadium. The oxides per se or those produced by reduction or decomposition of other vanadium compounds are preferred.

*Columbium*

A properly prepared carrier may be ground and sized to produce granules of relatively small mesh of the approximate order of from 4 to 20 and these caused to absorb compounds which will ultimately yield compounds of columbium on heating to a proper temperature by stirring them with warm aqueous solutions of soluble columbium compounds, such as for example the mixed fluoride of columbium and potassium already mentioned having the formula $CbOF_2.2KF.H_2O$, which is sufficiently soluble in water to render it utilizable as a source of columbium catalyst. Other soluble compounds which may be used to form catalytic deposits containing columbium are the various alkali metal columbates. Still other compounds of columbic acids, including salts of the alkaline earth and heavy metals, may be distributed upon the carriers by mechanical mixing either in the wet or the dry condition. As a rule the lower oxides are the best catalysts. The oxide resulting from the decomposition of such compounds as the pentahydroxide is for the most part the pentoxide $Cb_2O_5$. This oxide, however, is reduced to a definite extent by hydrogen or by the gases and vaporous products resulting from the decomposition of the hydrocarbons treated in the first stages of the process, so that the essential catalysts for the larger portion of the period of service are evidently the lower oxides $CbO_2$, $Cb_2O_3$, and CbO.

*Tantalum*

Compounds of tantalum, such as for example, the pentoxide $Ta_2O_5$ and the tetroxide $Ta_2O_4$, and possibly the sesquioxide $Ta_2O_3$, which result from the reduction of the pentoxide are particularly efficient as catalysts for the present types of reactions but the invention is not limited to their use but may employ any of the catalytically active compounds of tantalum. Tantalum fluoride and the double fluoride of tantalum and potassium having the formula $TaK_2F_7$ are soluble in water and may be conveniently used in aqueous solution as ultimate sources of the oxides which result from the ignition of the precipitated hydroxide to form the pentoxide and the partial reduction of this oxide by hydrogen or the gases and vapors in contact with the catalyst in the normal operation of the process. The tantalum pentahydroxide may be precipitated from a solution of the double fluoride by the use of ammonium or alkali metal hydroxides or carbonates as precipitants, the hydrate being later ignited to form the pentoxide, which may undergo some reduction as already stated.

Aluminum oxide, a particularly good support for use in the manufacture of catalysts for the process may be obtained from natural aluminum oxide minerals or ores such as bauxite or carbonates such as Dawsonite by proper calcination, or it may be prepared by precipitation of aluminum hydrate from solutions of aluminum sulfate or different alums, and dehydration of the precipitate of aluminum hydroxide by heat, and usually it is desirable and advantageous to further treat it with air or other gases, or by other means to activate it prior to use.

Two hydrated oxides of aluminum occur in nature, to wit, bauxite having the formula $Al_2O_3.2H_2O$ and Diaspore $Al_2O_3.H_2O$. In both of these oxides iron sesqui-oxide may partially replace the alumina. These two minerals or corresponding oxides produced from precipitated alu-

minum hydroxide are adaptable for the manufacture of the present type of catalysts and in some instances have given the best results of any of the base compounds whose use is at present contemplated. The mineral Dawsonite having the formula $Na_2Al(CO_3)_2.2Al(OH)_3$ is another mineral which may be used as a source of aluminum oxide.

It is good practice in the final steps of preparing aluminum oxide as a base catalyst to ignite for some time at temperatures within the same approximate range as those employed in the process, to-wit, from 400 to 850° C. This probably does not correspond to complete dehydration of the hydroxides but apparently gives a material of good strength and porosity so that it is able to resist for a long period of time the deteriorating effects of the service and regeneration periods to which it is subjected. In the case of the clays which may serve as base catalytic materials for supporting promoters, the better materials are those which have been acid-treated to render them more siliceous. These may be pelleted or formed in any manner before or after the addition of the promoter catalyst since ordinarily they have a high percentage of fines. The addition of certain of the promoters, however, exerts a binding influence so that the formed materials may be employed without fear of structural deterioration in service.

It is particularly advantageous to employ the type of aluminum oxide known as gamma-alumina, by which is meant the modification obtained by the dehydration of the monohydrate termed böhmite (AlO.OH) or the tri-hydrate $Al(OH)_3$ termed hydrargillite or gibbsite, when occurring in nature. It is characterized by definite crystallographic properties and can be readily distinguished from the large number of other modifications of alumina, such as alpha, beta, epsilon, zeta, etc., by its X-ray difraction pattern. The gamma-alumina crystallizes in the cubic system with the edge of the unit cube being about 7.9 Angstrom units.

Our investigations have also definitely demonstrated that the catalytic efficiency of such substance as alumina, magnesium oxide, and clays which may have some catalytic potency in themselves is greatly improved by the presence of compounds of the preferred elements in relatively minor amounts, usually of the order of less than 20 mol per cent of the carrier.

The most general method for adding the promoting materials is to stir the prepared granules of from approximately 4 to 20 mesh into solutions of salts which will yield the desired promoting compounds on ignition under suitable conditions. In some instances the granules may be merely stirred in slightly warm solutions of salts until the dissolved compounds have been retained on the particles by absorption or occlusion, after which the particles are separated from the excess solvent by settling or filtration, and then ignited to produce the desired residual promoter. In cases of certain compounds of relatively low solubility it may be necessary to add the solution in successive portions to the adsorbent base catalyst with intermediate heating to drive off solvent in order to get the required quantity of promoter deposited upon the surface and in the pores of the base catalyst. The temperatures used for drying and calcining after the addition of the promoters from solutions will depend entirely upon the individual characteristics of the compound added and no general ranges of temperature can be given for this step.

In some instances promoters may be deposited from solution by the addition of precipitants which cause the deposition of precipitates upon the catalyst granules. As a rule methods of mechanical mixing are not preferable, though in some instances in the case of hydrated or readily fusible compounds these may be mixed with the proper proportions of base catalysts and uniformly distributed during the condition of fusing or fluxing.

In regard to the relative proportions of carriers and catalysts it may be stated in general that the latter are generally less than 20 mol per cent of the total composites. The effect upon the catalytic activity of the base catalysts caused by varying the percentage of any given compound or mixture of compounds deposited thereon is not a matter for exact calculation but more one for determination by experiment. Frequently good increases in catalytic effectiveness are obtainable by the deposition of as low as 2% to 8% of a promoting compound upon the surface and in the pores of the base catalyst.

In operating the process the general procedure is to vaporize hydrocarbons or mixtures of hydrocarbons and after heating the vapors to a suitable temperature within the ranges previously specified to pass them through stationary masses of granular catalytic material in vertical cylindrical treating columns or banks of catalyst-containing tubes in parallel connection. Since the reactions are endothermic it may be necessary to apply some heat externally to maintain the best reaction temperature. After passing through the catalytic zone the products are submitted to fractionation to recover cuts or fractions containing the desired aromatic product with the separation of fixed gases, unconverted hydrocarbons, and heavier residual materials, which may be disposed of in any suitable manner depending upon their composition. Yields may obviously be increased by recycling unconverted materials, although this is not specifically characteristic of the present invention.

The following examples are given to indicate the character of the results obtainable by the use of the process but not with the intention of correspondingly limiting its proper scope.

*Example I*

The catalyst used consisted of activated alumina granules of approximately 10–20 mesh supporting about 15% by weight of vanadium oxide. The preparation was made by using the principles outlined in the foregoing specification. Cyclo-hexane vapors were passed over the bed of catalyst granules at a temperature of 525° C. at substantially atmospheric pressure at a rate corresponding to approximately 12 seconds contact time. In a once-through operation, a 25% yield of benzene was obtained and by recycling, an ultimate yield of 70% was possible. Tests for olefins in the products could be obtained, but there was no indication of isomerization reactions.

*Example II*

A catalyst comprising about 12% of columbium oxides supported upon a prepared granular silica was used to dehydrogenate methyl-cyclo-hexane, using a temperature of 530° C. and various times of contact. In the following table, the rate of

production of toluene in parts per 100 parts by weight of catalyst per hour is shown:

| Contact time, seconds | Toluene production, g. per hour/100 g. catalyst |
|---|---|
| 4.0 | 38.0 |
| 4.5 | 42.0 |
| 6.0 | 33.0 |

We claim as our invention:

1. A process for the dehydrogenation of naphthene hydrocarbons which comprises subjecting the vapors of said hydrocarbons to contact under dehydrogenating conditions with gamma alumina supporting a compound of a metal selected from those in the lefthand column of group V of the periodic table consisting of vanadium, columbium, and tantalum.

2. A process for the dehydrogenation of naphthene hydrocarbons which comprises subjecting the vapors of said hydrocarbons at a temperature within the approximate range of 400–650° C. to contact with gamma alumina supporting a compound of a metal selected from those in the lefthand column of group V of the periodic table consisting of vanadium, columbium, and tantalum.

3. A process for the dehydrogenation of naphthene hydrocarbons which comprises subjecting the vapors of said hydrocarbons at a temperature within the approximate range of 400–650° C. under a pressure of from atmospheric to 100 lbs. per square inch to contact with gamma alumina supporting a compound of a metal selected from those in the lefthand column of group V of the periodic table consisting of vanadium, columbium, and tantalum.

4. A process for the dehydrogenation of naphthene hydrocarbons which comprises subjecting the vapors of said hydrocarbons at a temperature within the approximate range of 400–650° C. under a pressure of from atmospheric to 100 lbs. per square inch for a time of 0.01–60 seconds to contact with gamma alumina supporting a compound of a metal selected from those in the lefthand column of group V of the periodic table consisting of vanadium, columbium, and tantalum.

5. A process for the dehydrogenation of naphthene hydrocarbons which comprises subjecting the vapors of said hydrocarbons at a temperature within the approximate range of 400–650° C. under a pressure of from atmospheric to 100 lbs. per square inch for a time of 0.01–60 seconds to contact with gamma alumina supporting a minor amount, of the order of less than 20% by weight, of a compound of a metal selected from those in the lefthand column of group V of the periodic table consisting of vanadium, columbium, and tantalum.

6. A process for the dehydrogenation of naphthene hydrocarbons which comprises subjecting the vapors of said hydrocarbons at a temperature within the approximate range of 400–650° C. under a pressure of from atmospheric to 100 lbs. per square inch for a time of 0.01–60 seconds to contact with gamma alumina supporting a minor amount, of the order of less than 20% by weight, of vanadium oxide.

7. A process for the dehydrogenation of methyl-cyclo-hexane to produce toluene therefrom which comprises subjecting the vapors of said methyl-cyclo-hexane to contact under dehydrogenating conditions with gamma alumina supporting a compound of a metal selected from those in the lefthand column of group V of the periodic table consisting of vanadium, columbium, and tantalum.

8. A process for the dehydrogenation of cyclohexane which comprises subjecting the vapors of the cyclo-hexane to contact under dehydrogenating conditions with gamma alumina supporting a compound of a metal selected from those in the lefthand column of group V of the periodic table consisting of vanadium, columbium, and tantalum.

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