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OXIDATION OF DICYCLIC HYDROCARBONS

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This invention relates to a vapor phase selective oxidation of dicyclic C_9 hydrocarbons to aromatic acids and anhydrides and specifically to catalytic oxidation of petroleum fractions obtained from vapor phase cracking in the presence of steam containing substantial amounts of indene and hydrindene to yield phthalic anhydride.

It is well known to the art that naphthalene (B. P. 218° C.) can be oxidized by various vapor phase processes to yield phthalic anhydride. It is further known that o-xylene (B. P. 144.5° C.) can likewise be converted to phthalic anhydride by somewhat similar oxidation procedures. However, these two types of reactants are available in limited quantities, insufficient for present day needs.

It has now been found that certain petroleum fractions which contain special types of hydrocarbons boiling in the range of 165–185° C. can be used as feed stock for vapor phase oxidation to phthalic anhydride in good yields. The C_9 hydrocarbons present in such a fraction have a variety of structures, but to a substantial extent they include dicyclic compounds represented by the unsaturated compound indene and by the partially saturated compound hydrindene which have five membered rings attached to a benzenoid nucleus.

It is especially advantageous that readily available mixtures of hydrindene and indene contain other components which also undergo oxidation favorable to the yields of phthalic anhydride. Cuts containing hydrindene or indene are obtained by fractionation of petroleum and more advantageously by fractionation of cracked products from a high-temperature steam-cracking of petroleum. A crude aromatic fraction boiling between 165° C. to 185° C. and containing substantial amounts of hydrindene and indene, for example, can be oxidized to good yields of phthalic anhydride. Such oxidizable fractions can be obtained, for instance, by the steam-cracking of gas oil, kerosene, or naphtha feed stocks. This cracking operation is carried out by vaporizing a suitable hydrocarbon feed stock, admixing the vapor with steam, and subjecting the mixture to a high temperature cracking operation, generally at temperatures of about 600–800° C. The hot cracked products are quenched and sent to a primary fractionating unit. This separates the product into a gas stream, a number of distillate fractions of various boiling ranges, and a tar stream. These various fractions are purified, dehydrated, and

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further fractionated into cuts of relatively narrow boiling ranges. Any particular cut will obviously contain the compounds whose boiling points fall in the boiling range of the fraction. The exact concentrations of the compounds in the fraction will depend on the composition of the feed stock to the cracking unit. A fraction may be selected which contains a maximum amount of the preferred compounds containing the indene structure. In using such mixtures, any oxidizable components are likewise converted to the acids as they normally yield under the operating conditions, while inert materials pass through the reaction zone unchanged and are easily separated from the acidic products later.

Certain coal tar fractions containing substantial amounts of indene and related hydrocarbons can also be used as the feed stock for the oxidation.

The oxidation may be carried out by any convenient procedure for vapor phase catalytic oxidations. Special kinds of construction materials are not required since corrosion troubles are negligible. The catalyst may be employed in a fixed bed or it may be of the moving bed or fluid flow type such as have been found especially advantageous in other catalytic operations. A transfer line reactor may offer special advantages.

The finely divided, fluidized oxidation catalyst is introduced into the bottom of the reaction zone by means of a stream of inert gaseous carrying medium. The catalyst is carried upward through the reaction zone into which the hydrocarbon feed is also introduced. Oxygen or air may also be introduced into the reaction zone either with the catalyst or separately. The oxidized products are removed as the outlet stream from the upper portion of the reactor. After passing through the reaction zone the catalyst particles are exposed to a stripping treatment, for example, by steam to remove products and unreacted feed. The stripped catalyst is passed continuously through a standpipe to the lower portion of the reactor and thence recycled through the reaction zone. This arrangement gives a valuable advantage in carrying out exothermic oxidations as heat can be removed from the catalyst while it is outside the heat generating reaction zone.

As catalysts for this reaction there may be used any of those commonly employed for catalytic oxidations. Among the best known are the vanadium containing catalysts. These may

be vanadium oxide alone or they may be mixtures of vanadium and other oxides as, for example, molybdenum oxide. Suitable promoters may be added to such catalysts.

These catalysts may be of the supported type, using as supporting agent some material which is inert to the reaction conditions. The catalyst may be of the formed type, such as the fluidized catalysts. An especially valuable form for use in such apparatus as the transfer-line reactor is a catalyst having the shape of microspheres. These spheres may be produced by heating the catalyst material to fusion followed by treatment to give the catalytic material the form of microspheres. These microspheres can be used satisfactorily for longer periods of time since they are not subject to the attrition and grinding difficulties inherent in other forms of catalyst particles.

The oxidation can be carried out either with or without the presence of an oxidizing gas in the reaction zone.

The oxidizing gas which is used may be any oxygen-containing gas. While pure oxygen can be used, it is preferable to add an inert diluent to insure better control and a smoother oxidation. Air, of course, is a very convenient and useful mixture. Synthetic mixtures can also be used in which oxygen is admixed with an inert gas such as nitrogen.

It is also possible to carry out the oxidation without diluting the hydrocarbon reactants by an oxygen-containing gas. Certain catalysts, in particular the higher oxides of vanadium may be employed as oxygen carriers which can be enriched with reactive oxygen in a zone completely separated from that in which reaction occurs. This type of reaction can be carried out in a number of ways. It is particularly well adapted for use in a modified transfer line type reactor.

If an oxidizing gas is used, it should be present in the feed mixture in such quantities as to provide a substantial excess over the hydrocarbons being oxidized. This tends to prevent tar formation and excessive decomposition to worthless by-products. It has been found preferable to operate the process using feed mixtures in which hydrocarbon is present at concentrations of 0 50 to 2.00 mole percent. The optimum concentration will depend somewhat on the specific substances being oxidized and on control of variables during the reaction. Any oxidizable feed which passes through unchanged may be recovered from the exit gases and recycled through the catalytic zone.

The temperature employed during the oxidation may be in the range of 400° C.–700° C. The temperature of the catalytic zone should be high enough to effect the desired conversion of feed to phthalic anhydride but not so high as to produce excessive combustion as this results in ultimate loss of product, contamination of the catalyst, and impurities which give expensive and unnecessary separation difficulties. An optimum range of temperature has been found to be 430° C.–480° C. This optimum obviously depends somewhat on type of apparatus, composition of feed, contact time, and other variables of the process.

The mixture of oxidizing gas and hydrocarbon feed should be contacted with the catalyst at such a rate as to be practical for commercial operation, allowing sufficient time for such conversion to phthalic anhydride as is most desirable. Too long an exposure to the catalyst tends to cause formation of over-oxidized products. It has been found preferable to operate the process at a catalyst contact time of about 0.1 to 1.0 second. Wide variations from these optimum conditions will give less satisfactory results. Any unreacted feed recovered in the exit gases may be recycled to the catalytic zone.

The invention will be described in more detail by the following examples which are intended to be illustrative only and in no way limitative.

Example 1

A feed consisting substantially of air and a vaporized petroleum fraction boiling 165°–185° C. such as can be obtained from high temperature refinery cracking operations and containing substantial amounts of indene and hydrindene was contacted with a vanadium oxide catalyst on a corundum support. Temperatures of from 430°–480° C. were maintained within the reaction zone. The concentration of hydrocarbon vapor in the feed mixture was about 0.5 to 1.0 mole percent and a catalyst contact time of about 0.4 second was used. The oxidized product may be recovered by any method such as by an air condenser. A satisfactory conversion of the hydrocarbon feed to phthalic anhydride was obtained.

Example 2

A mixture of hydrindene vapor and air was contacted with an oxidation catalyst composed of vanadium oxide supported on corundum and promoted by a small amount of a potassium salt. Temperatures of 430° C.–480° C. were maintained within the reaction zone. The concentration of hydrocarbon vapor in the feed mixture was about 0.5 to 1.0 mole percent. The mixture was exposed to the catalyst at the average rate of 2000–3000 volume of feed per volume of catalyst per hour with a catalyst contact time of about 0.1 to 1 second. The oxidized product may be recovered by any convenient method; for example, by air condensation. The product may be further separated and purified. A good yield of phthalic anhydride was obtained based on conversion of the hydrindene consumed.

Example 3

A mixture of indene vapor and air was contacted with an oxidation catalyst composed of vanadium oxide on corundum promoted by a small amount of potassium sulfate. The temperature was maintained within limits of 430° to 480° C. In general, the catalyst temperatures were somewhat higher, being in the range of 650°–700° C. The concentration of indene vapor in the feed mixture was about 0.5 to 1.0 mole percent and a contact time of from 0.1 to 1 second was used. The oxidized product may be conveniently recovered by condensation of the exit vapors and may be further separated and purified in any desired way. A conversion of about 70 mole percent of the indene to phthalic anhydride was thus obtained.

What is claimed is:

1. A catalytic, vapor phase process for the preparation of phthalic anhydride which comprises oxidizing a petroleum hydrocarbon fraction of boiling range 165–185° C. containing substantial amounts of hydrocarbons having the indene nucleus in the presence of a vanadium oxide catalyst at temperatures above 400° C.

2. A catalytic process for the preparation of

phthalic anhydride which comprises passing a gaseous mixture of oxygen and a petroleum fraction of boiling range 165°–185° C. containing substantial amounts of indene and hydrindene over a vanadium oxide catalyst at temperatures of 400°–700° C.

3. A catalytic, vapor-phase process as described in claim 2 in which the catalyst is vanadium oxide supported on corundum and promoted with potassium sulfate and the catalyst contact time is 0.1 to 1 second.

4. A catalytic process for the preparation of phthalic anhydride which comprises contacting a gaseous mixture containing oxygen and a hydrocarbon having a benzenoid ring fused to a five carbon atom ring selected from the group consisting of indene and hydrindene with a vanadium oxide catalyst at a temperature above 400° C.

5. A catalytic process for the preparation of phthalic anhydride which comprises passing a mixture of indene vapor and air over a vanadium oxide catalyst at temperatures of 400°–700° C.

6. A catalytic process as described in claim 5 in which the catalyst is vanadium oxide supported on corundrum and promoted with potassium sulfate and the catalyst contact time is 0.1 to 1 second.

7. A catalytic process for the preparation of

phthalic anhydride which comprises passing a mixture of hydrindene vapor and air over a vanadium oxide catalyst at temperatures of 400°–700° C.

8. A catalytic process as described in claim 7 in which the catalyst is vanadium oxide supported on corundum and promoted with potassium sulfate and the catalyst contact time is 0.1 to 1 second.

9. A process which comprises converting indene to phthalic anhydride by partial oxidation of said indene in vapor phase with an oxygen-containing gas and in the presence of a vanadium oxide catalyst, and recovering phthalic anhydride formed by said oxidation from the partial combustion mixture.

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