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NON-CATALYTIC DEMETHYLATION OF
TOLUENE

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This invention relates to a process for the demethylation of aromatic hydrocarbons, and more particularly relates to a process for the demethylation of methyl substituted aromatic hydrocarbons.

Dealkylation of a large number of compounds has been described. However, dealkylation of alkyl aromatic hydrocarbons becomes increasingly difficult as the size of the alkyl group decreases, so that in cleaving the methyl group it has heretofore been considered necessary to employ a catalyst to achieve the desired result. Catalytic methods for removing low molecular weight alkyl groups, such as the methyl group, from aromatic hydrocarbons usually employ as the catalyst a member of the iron group or an oxide thereof, such as iron, nickel, cobalt, or an oxide thereof. In such processes, however, substantial quantities of gas and coke are frequently formed and the catalyst is relatively rapidly deactivated.

An object of the present invention is to provide a process for cleaving the methyl group from a methyl substituted aromatic hydrocarbon. A particular object is to provide a process for the demethylation of toluene without the necessity of employing a catalyst. Other objects will be apparent from the following specification.

It has now been found that by subjecting a mixture of a methyl substituted aromatic hydrocarbon and an acyclic hydrocarbon having from 2 to 5 carbon atoms to a relatively high temperature in the absence of catalytic materials under correlated conditions of temperature, contact time and mole ratio of acyclic hydrocarbon to methyl substituted aromatic, the methyl radical is cleaved from the aromatic nucleus. For example, using toluene as the methyl substituted aromatic, benzene and methane are formed in good yields. The acyclic hydrocarbon employed is converted to other compounds, depending on the particular acyclic compound employed, as hereinafter discussed.

For convenience, the process of the invention is described herein using toluene as illustrative of the methyl substituted aromatic hydrocarbons that can be employed; other methyl substituted aromatic hydrocarbons that can be employed are described hereinafter. By "contact time," as used herein, is meant the time during which the mixture of toluene and acyclic hydrocarbon is maintained at a temperature within the range defined for dealkylation, and is the ratio of the free volume of the reactor to the volume of gas passing through the reactor at the temperature and pressure employed per unit time. To illustrate correlated conditions of demethylation in accordance with the process of the present invention, a mixture of propane and toluene having a mole ratio, propane to toluene, of 2.5 is heated to a temperature of about 675° C. for about 20 seconds at a pressure of about 300 pounds per square inch gauge (p. s. i. g.) to produce benzene, propylene and methane as substantially the sole products.

Acyclic compounds which can be employed are the non-cyclic hydrocarbons having from 2 through 5 carbon

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atoms per molecule. Paraffins such as ethane, propane, n-butane, isobutane and the pentanes give good results, as do the corresponding olefinic hydrocarbons such as propylene, butene-1, butene-2 and butadiene-1,3. When a paraffin is employed as the acyclic hydrocarbon, it appears that the paraffin is converted to a corresponding olefin. For example, when ethane is employed, ethylene appears as a product and when isobutane is employed, isobutylene appears as a product. When an olefin is employed as the acyclic compound, it appears that the olefin undergoes polymerization to the dimer. For example, ethylene is converted in the process to butylene.

The use of propylene as the acyclic hydrocarbon forms a preferred embodiment of the process. When a mixture of propylene and toluene is subjected to the reaction conditions herein described, benzene, methane and diallyl (hexadiene-1,5) appear as products; the so-formed diallyl can cyclize to form benzene and hydrogen and in this manner the yield of benzene is enhanced. When propane or other paraffin is employed, the propylene or other olefin formed in the process, as above described, can undergo the reactions as described for the initial use of olefins.

In order to obtain satisfactory results, it is essential that the temperature be maintained above about 500° C. and not above about 800° C. At temperatures below 500° C., substantial reaction does not occur, whereas at temperatures above 800° C., cleavage, polymerization and other undesired reactions involving olefins introduced or formed in the reaction are observed. The time during which the mixture of toluene and acyclic hydrocarbon is maintained at the elevated temperature, i. e., the contact time, must be within the range of from 2 to 60 seconds and preferably is within the range of from 5 to 40 seconds. At longer contact times, rupture of the aromatic nucleus, polymerization of the olefin, or other undesired reactions may occur, whereas at contact time shorter than about 2 seconds, dealkylation to a practical extent is not observed. It is preferred to employ relatively short contact times with relatively high temperatures, e. g. a contact time of 10 seconds at a temperature of 750° C. and a relatively long contact time with relatively low temperatures, e. g. a contact time of 20 seconds at 650° C. It is essential, however, to maintain the temperature and contact time within the defined limits.

The mole ratio of acyclic hydrocarbon to aromatic must be maintained within the range of from 0.5:1 to 20:1. When the acyclic hydrocarbon is a paraffin hydrocarbon, it is preferred to maintain the mole ratio of paraffin to toluene within the range of from 1:1 to 20:1. When the acyclic hydrocarbon is an olefin, it is preferred to maintain the mole ratio of olefin to toluene within the range of about 0.5:1 to 10:1. The total pressure under which the process should be performed can be varied from about 75 to 700 p. s. i. g. At lower pressures, say about atmospheric pressure, considerable quantities of high boiling materials are formed.

As above described, methyl substituted aromatic hydrocarbons other than toluene can be employed in the process with good results. For example, o-xylene; m-xylene; p-xylene; 1,2,3-trimethylbenzene; 1,2,4-trimethylbenzene; 1,3,5-trimethylbenzene; alpha-methylnaphthalene; beta-methylnaphthalene, the dimethylnaphthalenes, and homologues thereof which are methylated aromatic hydrocarbons give good results in the process. With polymethyl aromatic hydrocarbons, it is possible to remove one or more of the methyl groups in a single pass. Relatively severe conditions, e. g. relatively high temperatures and long contact times within the limits herein defined, favor the removal of more than one methyl group from such polymethyl aromatic hydrocarbons. Aromatic hydrocarbons having higher alkyl substituent

groups are not operable in the process because such groups, by cleavage, cause side reactions to occur to a substantial extent, in some instances to the practical exclusion of demethylation.

In order to illustrate an embodiment of the process, a mixture of ethane and toluene having a mole ratio of ethane to toluene of 2:1 is continuously passed through a heated reactor maintained at a temperature of 600° C., the pressure being about 250 p. s. i. g. and the rate of flow such that a contact time of 10 seconds is maintained. In a single pass, there is obtained about a 55% conversion of the toluene, the products being benzene, methane and ethylene. When the propylene is substituted for ethylene in the above process, substantially the same results are obtained, the products being benzene, methane and hydrogen. The hydrogen apparently is formed in the cyclization of diallyl, formed by the dimerization of propylene to benzene.

When other acyclic hydrocarbons and/or methyl substituted aromatic hydrocarbons are employed in the process within the limitations above described, substantially equivalent results are obtained, the foregoing example being presented to illustrate an embodiment of the process of the invention.

In operating the process of the invention within the limitations as above set forth, substantially no coke is formed and rupture of the aromatic nucleus is not observed. It is important, however, that the process be conducted in the absence of catalytic materials, such as the iron group metals or oxides thereof, such as iron, nickel, cobalt and silica-alumina, silica-zirconia, and the like, since such catalytic materials cause undesired cracking and polymerization reactions.

The invention claimed is:

1. Process for the demethylation of toluene which comprises heating, at a pressure of from 75 to 700 p. s. i. g. in the absence of catalytic materials, a reaction mixture consisting of toluene and an acyclic hydrocarbon having from 2 to 5 carbon atoms to within the temperature range of from 500° C. to 800° C., and maintaining said mixture within said temperature range for from 2 to 60 seconds, wherein the mole ratio of acyclic hydrocarbon

to toluene is from 0.5:1 to 20:1, whereby said toluene is demethylated.

2. Process according to claim 1 wherein said acyclic hydrocarbon is ethane.

3. Process according to claim 1 wherein said acyclic hydrocarbon is propane.

4. Process according to claim 1 wherein said acyclic hydrocarbon is a butane.

5. Process according to claim 1 wherein said acyclic hydrocarbon is propylene.

6. Process according to claim 1 wherein said acyclic hydrocarbon is butylene.

7. Process for the demethylation of a methyl substituted aromatic hydrocarbon which comprises heating, at a pressure of from 75 to 700 p. s. i. g. in the absence of catalytic materials, a reaction mixture consisting of said aromatic hydrocarbon and an acyclic hydrocarbon having from 2 to 5 carbon atoms to within the temperature range of from 500° C. to 800° C., wherein the mole ratio of acyclic hydrocarbon to said aromatic hydrocarbon is from 0.5:1 to 20:1, whereby said aromatic dehydrocarbon is demethylated.

8. Process according to claim 7 wherein said aromatic hydrocarbon is a xylene.

9. Process according to claim 7 wherein said aromatic hydrocarbon is a trimethylbenzene.

10. Process according to claim 7 wherein said aromatic hydrocarbon is a methyl-naphthalene.

11. Process according to claim 7 wherein said aromatic hydrocarbon is a dimethyl-naphthalene.

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