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CATALYTIC DEALKYLATION OF AROMATIC HYDROCARBONS

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The present invention relates to an improved method for the production of lower molecular weight aromatic hydrocarbons by dealkylation of higher molecular weight homologues, and is particularly concerned with the production of lower molecular weight aromatic hydrocarbons by dealkylation of higher molecular weight homologues boiling approximately in the gasoline range. The invention is especially concerned with the production of benzene by the catalytic dealkylation of methyl- and ethyl-substituted benzene homologues.

Among the objects of the invention is the provision of a highly selective dealkylation process capable of producing high yields of the desired lower molecular weight aromatic hydrocarbons while maintaining at a minimum the occurrence of accompanying side reactions which tend to produce coke and other products at the expense of the desired aromatic hydrocarbons.

In processes described in the art for the production of dealkylated aromatic hydrocarbons, involving superatmospheric pressure and temperature of about 900 to 1100° F. in the presence of added hydrogen, catalysts such as chromia and molybdena supported on carrier materials such as alumina and diatomaceous earth have been suggested for the dealkylation of alkyl-substituted aromatic hydrocarbons. While under the conditions advocated in these previously described processes, dealkylation of alkyl-substituted aromatic hydrocarbons present in the stock charged to dealkylation is stated to take place, side reactions generally occur to a substantial extent. These side reactions involve cracking of parts of the charge and polymerization of olefinic hydrocarbons in the reaction zone. They involve, also, undesirable disproportionation reactions. They also cause the formation of significant quantities of undesirable side reaction products, including coke, in sufficient amounts to limit the practical on-stream operating period and to require frequent regeneration of the catalyst. The extent to which such side reactions take place in these dealkylation processes is evidenced by the reported liquid product recoveries which are in the order of about 80 to 88 percent by weight. In other related processes described to involve superatmospheric pressure and temperature of about 350° to 750° F. in the presence of added hydrogen, catalysts such as nickel supported on carriers such as kieselguhr have been proposed to dealkylate selected alkyl-substituted aromatic hydrocarbons such as isopropylbenzene and xylenes. These processes advocated lower tem-

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peratures and the reported yields of dealkylated product per pass were lower than in the case of the first-mentioned processes. None of the above-discussed processes reported the production of substantial yields of benzene from the higher benzene homologues, thus clearly illustrating the difficulty of selectively and completely removing methyl and ethyl substituents from the benzene ring.

In accordance with the present invention, alkyl-substituted aromatic hydrocarbons, particularly monocyclic alkyl-substituted aromatic hydrocarbons, are selectively dealkylated to lower molecular weight aromatic hydrocarbons, especially benzene, under dealkylating conditions designed to favor greatly the desired dealkylation reaction, and considerably reduce or eliminate undesirable side reactions. This desirable result is achieved by carrying out the dealkylation process under carefully chosen conditions and in the presence of particularly selected catalysts which tend to promote dealkylation reactions but have no significant tendency to promote undesirable side reactions either by virtue of the catalysts' inherent properties or by reason of special catalyst treatments described below effective in eliminating or reducing such tendencies of the catalyst.

The supported catalysts used in the dealkylation process of the present invention comprise a carrier having a high surface area, generally in excess of 50 square meters per gram (as determined by the method of Brunnauer, Emmett and Teller described in the Journal of the American Chemical Society, vol. 60, pages 309 et seq. (1938)), and adapted to extensive and uniform distribution of the dehydrogenative material thereon. Also, the carrier material used is characterized by having no appreciable activity, either alone or in composition with the minor amounts of dehydrogenative components employed, less than about 15 per cent by weight of the carrier, in promoting polymerization-depolymerization reactions of hydrocarbons under dealkylating conditions.

As pointed out above, this latter characteristic of the carrier material may be inherent in the carrier or imparted thereto by means of a special conditioning or inactivating treatment. An example of a preferred inherently inactive carrier material is magnesia. Titania and silica gel also are members of this class of carrier materials. Certain natural materials, such as diatomaceous earth and pumice, while inherently, relatively inert catalytically, do not provide the high sur-

face area required for the dehydrogenative materials employed in catalysts used in the dealkylation process of the invention and are, therefore, not recommended for use therein.

Activated alumina is an example of a preferred carrier material of the class requiring a special conditioning treatment to impart thereto the required inactivity characteristic. While heat treated alumina and commercial "activated alumina" are usually not regarded as cracking catalysts in that they do not produce acceptable yields of gasoline in cracking of gas oils or the like, these materials do demonstrate appreciable catalytic activity in promoting polymerization and depolymerization of olefinic hydrocarbons and polymers, respectively. Since olefinic hydrocarbons are necessarily produced to greater or less extent, in the various stages of the mechanisms of dehydrogenation and other hydrocarbon conversion reactions, this tendency of alumina to promote polymerization and depolymerization reactions, even though small, becomes a very significant factor from the standpoint of introducing undesirable side reactions. The relative importance of this factor is readily understood in connection with the formation of coke on the catalyst, which formation appears at least to considerable extent to result from the deposition on the catalyst of high molecular weight polymers. In addition, the uncontrolled splitting of higher molecular weight olefins and polymers not directly forming coke results in side reaction products of the type and in quantities which the practice of this invention avoids.

The inactivation of catalyst carrier materials, such as activated and gamma aluminas for example, is effected by treating the support with an aqueous solution of an alkaline earth compound, particularly a solution of a magnesium or calcium salt. The treatment is generally designed to introduce into the carrier material an amount of salt equivalent to preferably about 0.1 to 2 per cent of alkaline earth metal oxide by weight based on the carrier. The treated carrier is freed of extraneous salts as by water washing and is then dried at about 200° F. and may be calcined, but is not heated to such high temperatures as to effect transformation of alumina to a so-called "beta" form. The deactivating effect of this treatment is often noticeable when as little as 0.05 per cent of magnesia, for example, is incorporated in an alumina carrier in the manner described above. Amounts of incorporated magnesia above about 2 to 3 per cent by weight of the alumina do not appear to have any added deactivating effect upon the alumina and may often be undesirable. Also suitable for deactivating the catalyst carrier material to substantially remove the cracking function, but not necessarily with equal quantitative effect, are the alkali metal oxides, particularly sodium oxide, when incorporated in the alumina in a manner similar to that described in the case of the alkaline earth metal oxides, and in approximately the same percentages.

It is preferable to incorporate the magnesia or other alkaline earth or alkali metal compound in the carrier before incorporating the hydrogenative material, such as a metal or metal oxide. For example, catalysts prepared by treating a composite of aluminaceous carrier and hydrogenative molybdena, with magnesia in the manner described above, do not have the high degree of selectivity and completeness of dealkylation that is observed with the preferred catalysts.

Among the catalytic dehydrogenative materials

that can be employed in the carrier materials of the invention to produce the composite catalysts used in the dealkylation process of the invention are the metals of group VI α of the periodic system including molybdenum and chromium oxides, and noble metals of the platinum-palladium group.

The dealkylation catalysts containing dehydrogenative materials, such as molybdena (molybdenum oxide) supported on a carrier, can be prepared by dipping the inactive or inactivated carrier material into a solution of a soluble molybdenum compound, such as ammonium molybdate, to cause some of the solution to be sorbed by the carrier, and then drying and decomposing the molybdenum compound to molybdena. The amount of molybdena thus incorporated in the carrier material should generally be less than about 15 per cent, and preferably less than about 12 per cent by weight based on the final catalyst composite.

In the case of the noble metal catalysts, the platinum, or other noble metal component, is generally employed in the catalyst in amounts less than about 2 percent by weight of the carrier (water free basis), and preferably in the range of about 0.05 to 1 percent by weight of the carrier. The metal can be added to the carrier by impregnating the inactive or inactivated carrier with an aqueous suspension of the metal oxide and then reducing the oxide to the free metal; or by dipping the carrier into a solution of a soluble compound of the metal, and then drying and decomposing the metal compound taken up by the carrier to the free metal or oxide. In the latter case the oxide is, of course, subsequently reduced to the free metal.

The conditions selected for the specific dealkylation reaction resulting in the production of benzene and lesser amounts of lower benzene homologues include temperatures preferably not below about 800° to 900° F. and as high as 1000° F., or higher. Temperatures below about 800° F. are not recommended because at these lower temperatures hydrogenation of aromatic hydrocarbons to naphthene hydrocarbons tends to occur with consequent reduction in yield of desired aromatics. The selected dealkylation conditions also include pressures preferably not above about 1000 pounds per square inch and as low as about 100 pounds per square inch, or lower. Pressures above 1000 pounds per square inch may be used but better results are obtained at the lower pressures. More particularly, the conditions for the more specific and relatively more complete removal of methyl or ethyl substituents from the benzene ring include temperatures in the range of about 900° to 1000° F., pressures in the range of about 100 to 800 pounds per square inch, space rates of about 3 (liquid vols. oil/hr./vol. cat.) or less, preferably 2 or less, and hydrogen to oil ratios in the range of about 3 to 10 moles hydrogen per mole of oil, preferably a ratio of about 4 to 1 moles hydrogen per mole aromatic hydrocarbon charge.

The dealkylation process of the invention is particularly designed to remove more completely and more selectively alkyl substituents from alkyl-substituted aromatic hydrocarbons than in the case of previous known dealkylation processes discussed above, and is particularly adapted to dealkylate alkyl-substituted monocyclic aromatic hydrocarbons, especially methyl- and/or ethyl-substituted benzene hydrocarbons, and more especially toluene and xylenes. The demethan-

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ation of toluene and xylene charge stocks takes place with relatively high yields per pass, with negligible coke or other by-product formation, and with exceptionally high liquid product recoveries. As a result of these unique features of the process, the dealkylated portion, e. g. benzene, of the recovered liquid product is separated from the undealkylated portion of the liquid product by a relatively simple operation, such as fractional distillation, and the undealkylated portion can be recycled repeatedly through the dealkylation stage of the process together with added fresh charge. Since negligible coke formation takes place in the process, the frequent catalyst regeneration required by previous dealkylation processes is eliminated, and on-stream periods of several weeks or more are possible. Such operation by virtue of the high selectivity and high degree of completeness of the present dealkylation process results in unusually high yields of the desired low molecular weight aromatic hydrocarbons.

The instant dealkylation process is especially adapted to the treatment of various narrow boiling hydrocarbon fractions rich in aromatic hydrocarbons boiling in the toluene and xylene range. The treatment of these narrow fractions, which will also include ethyl benzene, by the instant process, by virtue of the advantages and features pointed out above, results in the production of unusually high yields of demethanated aromatic hydrocarbons, and especially good yields of benzene. The production of benzene in good yields from toluene is, of course, a much more difficult operation than that of the production of toluene from xylenes. The success of the instant process in the more difficult operation of demethanation of toluene is a measure of the greater success of the process of the invention in the demethanation or the dealkylation of other methylated or alkylated aromatic hydrocarbons, respectively.

The present process is also applicable to greater advantage, for the reasons given above, to the dealkylation of alkyl-substituted aromatic hydrocarbons contained in various naphtha charge stocks such as straight run gasoline, catalytically cracked distillate, distillates from thermal cracking, and the like, as well as products and fractions from hydrogenative reactions.

The following example illustrates the method of preparation of a typical catalyst, and the method of use of the catalyst in the dealkylation process of the invention.

Example

Commercial activated alumina pellets (2.59 kg.) were treated with a 20 percent magnesium chloride hexahydrate solution by soaking the pellets in about 4 kg. of the solution for about 30 minutes. During the soaking period the pellets were stirred several times and the pH of the solution changed from an initial value of 5.8 to a final value of 7.0. The soaked pellets were washed free of chlorides and were dried overnight at 200° F. The dried product was dipped for about 30 minutes in a solution of ammonium molybdate containing about 1.12 kg. of ammonium molybdate in 3.5 liters of solution. The treated product was drained and dried for 3 hours at 200° F., and finally heat treated at 1050° F. for 2 hours. Before being placed on stream, hydrogen was passed over the catalyst to reduce the molybdenum to lower valence forms. The final catalyst contained an analysis, approximately

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9.9 percent molybdena, 0.1 percent magnesia and 90 per cent alumina by weight.

The catalyst thus prepared was used in demethylating toluene to benzene at several different pressures and liquid space velocities at 950° F., in the presence of added hydrogen in the ratio of 4.0 mols hydrogen to 1.0 mol toluene, over a period of one hour. The following table is a summary of the data obtained:

Run Number.....	1	2	3
Pressure, p. s. i.....	800	300	100
Liquid Space Velocity, V./V./Hr.....	2	2	1
Liquid Recovery, Vol. Percent.....	98.4	97.4	93.6
Liquid Recovery, Wt. Percent.....	97.9	95.3	93.5
Benzene Yield, Wt. Percent of Feed.....	7.9	10.9	11.3
Toluene Demethanation, Wt. Percent.....	9.3	12.8	13.3

The data indicate that dealkylation proceeds more satisfactorily at moderate pressures in the range of about 100 to 500 pounds per square inch than at higher pressures in the range of about 500 to 1000 pounds per square inch. The amount of coke and other side reaction products produced in these runs was negligible. Thus substantially all of the toluene feed converted by the reaction was demethanated to produce benzene in contradistinction to previous known dealkylation processes in which appreciable cracking takes place and relatively lower liquid recoveries are obtained due to the production of appreciable amounts of coke and cracked gases.

Similar results as to desired dealkylation selectivity and desired dealkylation completeness, resulting in high yields of the desired dealkylated aromatic hydrocarbon, are obtained when using noble metals of the platinum-palladium group as the dehydrogenative component on an inactive or inactivated catalyst carrier material; and also when charging the various other methyl-, ethyl- and alkyl-substituted aromatic hydrocarbon-containing fractions and materials described above, as the feed materials in the described dealkylation process of the invention.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim as my invention:

1. The method of producing benzene comprising contacting a charge stock containing toluene in the presence of added hydrogen with a catalyst comprising an aluminaceous carrier of attenuated cracking activity and containing less than 15% (determined as MoO₃) by weight of the catalyst of molybdenum oxide, said catalyst being one prepared by impregnating an activated alumina with magnesia and calcining the impregnated alumina at elevated temperature below that effecting transformation to "beta" form followed by incorporation of the molybdenum oxide; said contacting being carried out at a temperature in the range of about 900 to 1000° F., a pressure in the range of about 100 to 800 pounds per square inch, a hydrogen to toluene ratio of about 4 moles hydrogen per mole toluene and a space rate in the range of about 1 to 2 liquid volumes of toluene per hour per volume of catalyst.

2. The method of producing benzene which comprises contacting a charge stock comprising methyl substituted benzene hydrocarbons under a superatmospheric partial pressure of hydrogen with a catalyst composed of activated alumina

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of attenuated cracking activity containing a minor quantity of a dehydrogenating component, said contacting being performed under conditions favoring dealkylation of methyl substituted hydrocarbons in the charge stock and including pressure in the range of about 190-800 pounds per square inch and temperature in the range of about 900-1000° F., and recovering a benzene fraction from the product; said catalyst being prepared by impregnating an activated alumina with 0.1 to about 2% by weight of magnesia and calcining the impregnated alumina at elevated temperature below that effecting transformation to "beta" form, and thereafter incorporating in the magnesia-impregnated alumina up to 12% by weight (determined as MoO₃) of molybdenum oxide based on the final catalyst composite.

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