

[54] **HYDRODEALKYLATION PROCESS WITH PROMOTED GROUP VIB METALS AND PROMOTERS**

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[58] Field of Search **260/672 R**

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[57]

ABSTRACT

A process for the hydrodealkylation of alkyl-substituted aromatic hydrocarbons, including contacting the alkyl-substituted aromatic hydrocarbons with a catalyst comprising a metal of Group VIB of the Periodic System, such as chromium, molybdenum, and tungsten, and mixtures thereof, in an amount of about 5 to 15 per cent by weight of the finished catalyst, and a promoter selected from the group consisting of alkali metals, alkaline earth metals, rare earth metals, and mixtures thereof, such as potassium, rubidium, cesium, calcium, strontium, barium, cerium, thorium, etc., in an amount between about 1 to 10 percent by weight of the finished catalyst, at a temperature of about 1,050° to 1,200°F, a pressure of about 100 to 1,000 psig., a liquid hourly space velocity of about 0.1 to 5, and a hydrogen-to-hydrocarbon mole ratio between about 3 and 15 to 1.

8 Claims, No Drawings

HYDRODEALKYLATION PROCESS WITH PROMOTED GROUP VIB METALS AND PROMOTERS

RELATED APPLICATIONS

The present application is a continuation of Ser. No. 769,735, filed Oct. 22, 1968, now abandoned. Other related applications are Ser. No. 769,729, filed Oct. 22, 1968, now U.S. Pat. No. 3,700,745 and Ser. No. 769,733, filed Oct. 22, 1968, now U.S. Pat. No. 3,679,768.

BACKGROUND OF THE INVENTION

The present invention relates to a process for the hydrodealkylation of alkyl aromatics to the parent aromatic hydrocarbons. More specifically, the present invention relates to a process for the hydrodealkylation of alkyl aromatic hydrocarbons to the parent aromatic hydrocarbons, utilizing a unique catalyst system.

The hydrodealkylation of alkyl aromatics has been practiced for many years. The principal processes involve the conversion of toluene and like alkyl-substituted benzenes to benzene, and coal tar light oils and coal tar methyl naphthalene to benzene and naphthalene, respectively. These processes may be catalytic or non-catalytic in nature. The non-catalytic system which involves thermal dealkylation, in the presence of hydrogen, requires high temperatures and pressures. While the catalytic processes require lower temperatures and pressures, these temperatures and pressures are still quite high and therefore result in short catalyst life. Most commercial catalytic processes employ chromia-magnesia deposited on an alumina base as a catalyst. Since the development of this catalyst, there has really been no improvement in catalysts for this reaction.

It is therefore an object of the present invention to provide a new process for the hydrodealkylation of alkyl aromatic employing a novel catalyst system. In a more specific aspect, the present invention relates to a process for the hydrodealkylation of alkyl aromatics wherein catalysts which improve conversion are employed. Another and further object of the present invention is to provide a process for the hydrodealkylation of aromatics wherein catalysts of higher selectivity are utilized. A still further object of the present invention is to provide an improved process for the hydrodealkylation of alkyl aromatics wherein catalysts which reduce carbon lay-down on the catalyst are employed. A further object of the present invention is to provide an improved hydrodealkylation process for the hydrodealkylation of alkyl aromatics wherein novel catalysts are employed which permit operation at lower than conventional temperatures. Another and further object of the present invention is to provide an improved system for the hydrodealkylation of alkyl aromatics wherein catalysts are employed which permit the use of lower hydrogen partial pressures.

SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, alkyl aromatics are hydrodealkylated to their parent aromatic hydrocarbons by contacting the alkyl aromatic with a catalyst comprising a Group VIB metal oxide and an oxide selected from the group consisting of an alkali metal, an alkaline earth metal and a rare earth metal.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Suitable feedstocks for use in accordance with the present invention include toluene, polymethyl benzenes, coal tar light oils, coal tar methylnaphthalene concentrates, and bicyclic concentrates from light cycle oils and heavy reformates. Feedstock preparation includes fractionation to remove front ends or bottoms to thereby remove undesired fractions such as unsaturates, indanes and resinous materials. For example, it has been found the coal tar methylnaphthalene concentrates, as received from the coke oven, contain a large amount of contaminants, such as polymers, resins and free carbon. Distillation of such raw materials to yield a 90 percent overhead leaves these materials as a bottoms. Hydrogenation and hydrotreating of the overhead fraction removes sulfur, nitrogen and oxygen contaminants, but, due to the thermal instability of the feedstocks, a heavy resinous material is produced through thermal polymerization. Distillation of the hydrotreated product is required to remove these resins and thereby reduce carbon lay-down on the hydrodealkylation catalyst and reduce hydrogen consumption due to hydrocracking of the resins and polymers.

The processing conditions for the hydrodealkylation reaction of the present invention include a temperature between about 1,050° and 1,200°F, a pressure between about 100 and 1,000 psig., a liquid hourly space velocity between about 0.1 and 5, and a hydrogen-to-hydrocarbon mole ratio of about 3 to 15/1.

The catalysts to be employed in accordance with the present invention include metal oxides from Group VIB of the Periodic System, particularly chromium, molybdenum and tungsten. The promoters include alkali metal oxides of Group I of the Periodic System and, alkaline earth metal oxides of Group II of the Periodic System and the rare earth metals. Examples of materials of this nature which may be employed include potassium, rubidium, and cesium; magnesium, calcium and strontium, and cerium and thorium, etc. The active metal and the promoter are deposited on an inert oxide support, which preferably includes a high area alumina having a boehmite, bayerite, beta, or eta crystalline form, or other aluminas, silica-alumina, silica, silica-magnesia, silica-zirconia, alumina-magnesia, etc.

The optimum active metal content of the catalyst is about 5 to 15 percent by weight based on the final catalyst. The metal oxide promoter should be present in amounts of about 1 to 10 percent by weight.

The catalysts of the present invention may be prepared by well-known techniques in the art. Typical examples are coprecipitation or impregnation techniques. One may employ extrudates or pellets for impregnation or powders followed by pelletization or extrusion to yield the finished catalyst. The active metal and the promoter may be added through the use of water-soluble salts, such as their halides, nitrates, sulfates, acetates, etc. Easily hydrolyzed salts can be kept in solution without decomposition by employing appropriate inorganic acids.

The following examples illustrate methods of preparing the composite catalyst of the present invention.

Example I.

To 200 ml. of distilled water was added 15 g. of ce-

sium nitrate and 40 g. of chromic acid. This solution was added to 200 ml. of a boehmite alumina and after contact for fifteen minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250°F for one hour and calcined in air at 950°F for sixteen hours in a muffle furnace. This yielded a catalyst of the following composition:

10 percent Cr_2O_3 —4 percent Cs_2O — Al_2O_3 .

Example II.

To 500 ml. of distilled water was added 41 g. of cerous nitrate hexahydrate and 100 g. of chromic nitrate. This solution was added to 500 ml. of a bayerite alumina and after contact for fifteen minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250°F for one hour and calcined in air at 950°F in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

10 percent Cr_2O_3 —2 percent Ce_2O_3 — Al_2O_3 .

The following Table illustrates the advantages of the catalysts of the present invention as compared with a commercial chromia-magnesia on alumina catalyst.

TABLE I

[Feed: toluene. Standard conditions: 1,150° F., 500 p.s.i.g., 0.5 LHSV, 5/1 $\text{H}_2/\text{H}'\text{C}$]

	Run				
	1	2	3	4	5
Catalyst.....	12 Cr-2 Mg- Al_2O_3	10 Cr-4 K- Al_2O_3	10 Cr-4 Cs- Al_2O_3	12 Cr-4 Ce- Al_2O_3	12 Cr-4 Sr- Al_2O_3
Liquid recovery volume percent feed.....	84	83	80	77.0	83.0
Product distribution:					
< Benzene.....	0.8	0.7	0.9	1.2	0.2
Benzene.....	66.8	75.6	81.8	86.0	71.8
Toluene.....	32.4	23.7	17.3	13.8	28.0
Weight percent feed:					
Toluene conversion.....	72.8	80.2	86.2	89.4	76.5
Selectivity to benzene.....	92	93	92	89	94
Carbon on catalyst; weight percent feed.....	0.26	0.19	0.07	.005	.005

When reference is made herein to the Periodic System of elements the particular groupings referred to are as set forth in the Periodic Chart of the Elements, in "The Merck Index", Seventh Edition, Merck & Co., Inc., 1960.

We claim:

1. A process for hydrodealkylating alkyl aromatic hydrocarbons in a mixture comprising; contacting the hydrocarbon mixture with a catalyst consisting essentially of about 5 to 15 percent of an active metal of Group VIB of the Periodic System and about 1 to 10 percent by weight of a promoter metal selected from the group consisting of rubidium, cesium, calcium, strontium, barium, and thorium, and mixtures thereof, both impregnated on an alumina carrier selected from the group consisting of boehmite, bayerite, beta, alumina-magnesia, and mixtures thereof, under conditions sufficient to effect said hydrodealkylation reaction, including a temperature of about 1,050° to 1,200°F., a pressure of about 100–1,000 psig., a liquid hourly space velocity of about 0.1 to 5.0 and a hydrogen-to-hydrocarbon mole ratio between about 3 and 15 to 1.

2. A process in accordance with claim 1 wherein the promoter metal is calcium.

3. A process in accordance with claim 1 wherein the promoter metal is strontium.

4. A process in accordance with claim 1 wherein the promoter metal is barium.

5. A process in accordance with claim 1 wherein the promoter metal is thorium.

6. A process in accordance with claim 1 wherein the promoter metal is rubidium.

7. A process in accordance with claim 1 wherein the promoter metal is cesium.

8. A process in accordance with claim 1 wherein the alumina carrier is a gamma alumina.

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