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[54] **HYDRODEALKYLATION PROCESS WITH PROMOTED GROUP VIII METALS**

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

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[57] **ABSTRACT**

A hydrodealkylation process comprising contacting alkyl aromatic hydrocarbons with a catalyst, including an active Group VIII metal, such as, platinum, rhodium, palladium, ruthenium and nickel, a promoter selected from the group of alkali, alkaline earth and rare earth metals, such as, potassium, rubidium, cesium, calcium, strontium, cerium and thorium, and an inert oxide support such as, gamma aluminas, silica-alumina, silica, silica-magnesia, alumina-magnesia and silica-zirconia at a temperature of 1,050° to 1,200° F, a pressure of 100 to 1,000 psig., a liquid hourly space velocity of 0.1 to 5 and a hydrogen-to-hydrocarbon mole ratio of 3–15/1.

4 Claims, No Drawings

HYDRODEALKYLATION PROCESS WITH PROMOTED GROUP VIII METALS

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 aromatics employing a novel catalyst system. In a more specific aspect, the present invention relates to the 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, the process for the hydrodealkylation of aromatics is provided wherein an active metal of Group VIII is deposited on an inert oxide support and such Group VIII metal is promoted with a material selected from the group consisting of alkali metals, alkaline earth metals, rare earth metals, and mixtures of these materials.

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 methyl-

naphthalene 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 that 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 VIII of the Periodic System, particularly platinum, rhodium, palladium, ruthenium and nickel. The promoters include alkali metal oxides of Group I of the Periodic System, 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; 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 0.5 to 5 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 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 catalysts of the present invention.

EXAMPLE I

To 150 ml. of distilled water was added 2 g. of rhodium trichloride. This solution was added to 150 ml. of boehmite alumina pellets 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 1 hour and calcined at 950° F in air in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

$$1\%\ Rh—Al_2O_3.$$

A solution containing 150 ml. of distilled water and 20 g. of potassium nitrate was added to 150 ml. of $1Rh—Al_2O_3$ pellets and allowed to remain in contact for 15 minutes before decanting the unadsorbed liquid. The impregnated catalyst was dried at 250° F for 1 hour and calcined in air at 950° F for 16 hours in a muffle furnace. This yielded a catalyst of the following composition:

$$1\%\ Rh—4\%\ K_2O—Al_2O_3$$

EXAMPLE II

By employing the techniques and procedure outlined in Example I, other catalysts were prepared. A solution containing cesium nitrate was added to a boehmite alumina. Drying and calcination of this impregnated catalyst yielded the following composition:

$$4\%\ Cs_2O—Al_2O_3$$

An aqueous solution of chloroplatinic acid added to pellets of $4\%\ Cs_2O—Al_2O_3$ followed by drying and calcination yielded a catalyst of the following composition:

$$1\%\ Pt—4\%\ Cs_2O—Al_2O_3$$

USE OF CATALYSTS FOR HYDRODEALKYLATION

In order to illustrate the effectiveness of the catalysts of the present invention and the process for hydrodealkylation, a toluene feed was subjected to a temperature of 1,150° F, a pressure of 500 psig., a liquid hourly space velocity of 0.5, and a hydrogen-to-hydrocarbon mole ratio of 5:1, utilizing a commercial catalyst of chromia-magnesia on alumina as compared with certain of the catalysts of the present invention. The results of these Runs are shown in Table I. In a similar comparative run under exactly the same conditions, a topped, commercial, coal tar methyl naphthalene cut at 500° F and having the composition set forth in Table II was utilized with the results shown in Table II.

TABLE I

Run	1	2	3
Catalyst	$12Cr-2Mg-Al_2O_3$	$1Rh-4Cs-Al_2O_3$	$1Rh-4K-Al_2O_3$
Liquid Recovery Vol. % Feed	84	74	80
Product Distribution			
<Benzene	0.8	0.8	0.5
Benzene	66.8	97.5	96.0
Toluene	32.4	1.7	1.4
Wt. % Feed			
Toluene Conversion	72.8	98.8	98.9
Selectivity to Benzene	92	88	93
Carbon on Catalyst Wt. % Feed	0.26	0.03	0

TABLE II

Run	4	5
Catalyst	$12Cr-2Mg-Al_2O_3$	$1Rh-4Cs-Al_2O_3$
Product Distribution		
<Naphthalene	37.8	41.0
Naphthalene	59.0	53.8
Methylnaphthalene	1.4	0.5
Dimethylnaphthalene	2.9	4.7
Wt. % Feed		
Me Naphthalene Conversion	90	97
Carbon on Catalyst Wt. % Feed	1.32	0.82 Wt. %
(a)		
<Naphthalene		50.4
Naphthalene		30.4
Methylnaphthalene		13.4
Dimethylnaphthalene		5.8
>DMN		—

The catalysts of the present invention may be utilized with sulfur or none-sulfur containing feedstocks. Preferably, however, a feedstock containing small amounts of sulfur, for example 10 to 100 ppm., will minimize hydrocracking activity without impairing the hydrodealkylation activity of the catalyst.

The process of the present invention is further illustrated by the following examples in which a Group VIII metal was combined with an alkaline earth metal and with a rare earth metal and used as a catalyst for the process.

TABLE III

Hydrodealkylation of Toluene

Conditions: 1150°F, 500 PSIG, 0.5 LHSV, 5/1 $H_2H'C$
Feed: Toluene

Run	6	7
Catalyst	1 Pd — 4 Sr Al_2O_3	1 Pd — 4 Ce Al_2O_3
Liquid Recovery Vol. % Feed	91.3	88.8
Product Distribution		
<Benzene	0.2	0.6
Benzene	26.8	35.3
Toluene	73.0	64.1
Wt. % Feed		
Toluene Conversion	33.0	43.1
Selectivity to Benzene	89	87
Carbon on Catalyst Wt. % Feed	.002	.010

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.

What is claimed is:

1. A process wherein hydrodealkylating dealkylatable hydrocarbon materials is the dominant reaction, comprising: contacting the hydrocarbon materials with a catalyst consisting essentially of about 0.5 to 5 percent by weight of an active metal selected from the Group consisting of platinum, rhodium, palladium, ruthenium, and nickel and about 1 to 10 percent by weight of a promoting metal selected from the group consisting of cerium, thorium and mixtures thereof, both impregnated on an inert oxide carrier selected from the group consisting of alumina, silica, magnesia, zirconia, and mixtures thereof under conditions sufficient to effect said hydrodealkylation reaction, includ-

ing 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 gaseous hydrogen to inlet feed hydrocarbon mole ratio between about 3 and 15 to 1.

2. A process wherein hydrodealkylating dealkylatable methyl-substituted aromatic hydrocarbons is the dominant reaction comprising: contacting the hydrocarbons with a catalyst consisting essentially of about 0.5 to 5 percent by weight of an active metal selected from the group consisting of platinum, rhodium, palladium, ruthenium, and nickel and about 1 to 10 percent by weight of a promoting metal selected from the group consisting of cerium, thorium, and mixtures thereof, both impregnated on an inert oxide carrier selected from the group consisting of alumina, silica, magnesia, zirconia, 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 to 1,000 psig, a liquid hourly space velocity of about 0.1 to 5, and a gaseous hydrogen to inlet feed hydrocarbon mole ratio between about 3 and 15 to 1.

3. A process in accordance with claim 1 wherein the inert oxide carrier is a gamma alumina.

4. A process in accordance with claim 1 wherein the promoting metal is in its oxide form.

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