United States Patent [19]

Ransley

[11] **3,919,339**

[45] **Nov. 11, 1975**

[54] **HYDROGENOLYSIS/ISOMERIZATION PROCESS**

[75] Inventor: **Derek L. Ransley**, Berkeley, Calif.

[73] Assignee: **Chevron Research Company**, San Francisco, Calif.

[22] Filed: **Mar. 18, 1974**

[21] Appl. No.: **452,489**

[52] **U.S. Cl.** ..... **260/672 R**; 260/668 A; 260/672 T

[51] **Int. Cl.** **C07c 3/58**

[58] **Field of Search** ..... 260/672 R, 672 T, 668 A

[56] **References Cited**

UNITED STATES PATENTS

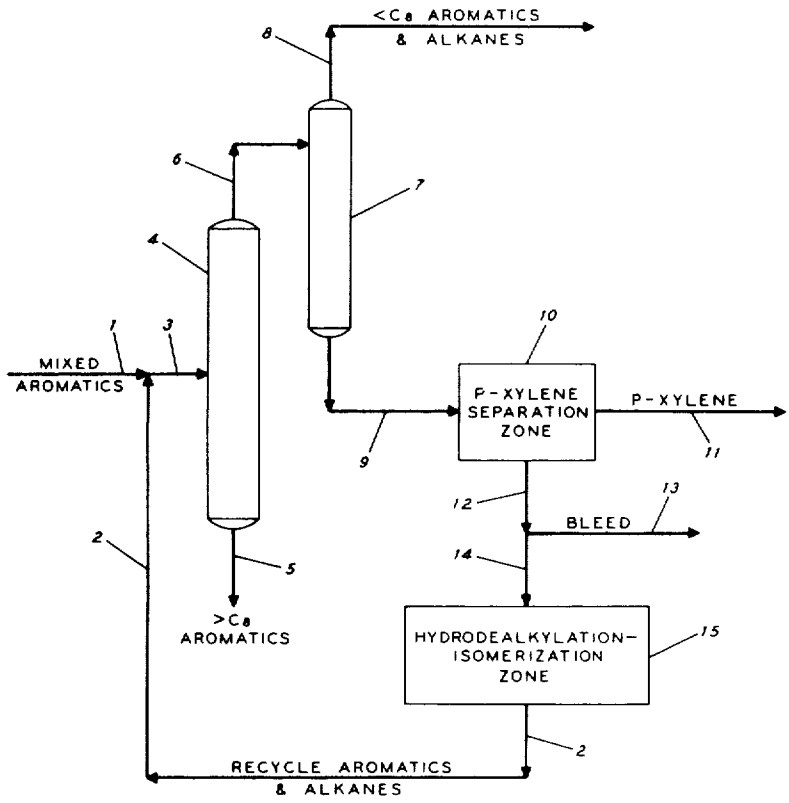
2,564,388	8/1951	Bennett et al.	260/668
3,088,984	5/1963	Oldenburg	260/668
3,548,017	12/1970	Hebert et al.	260/668

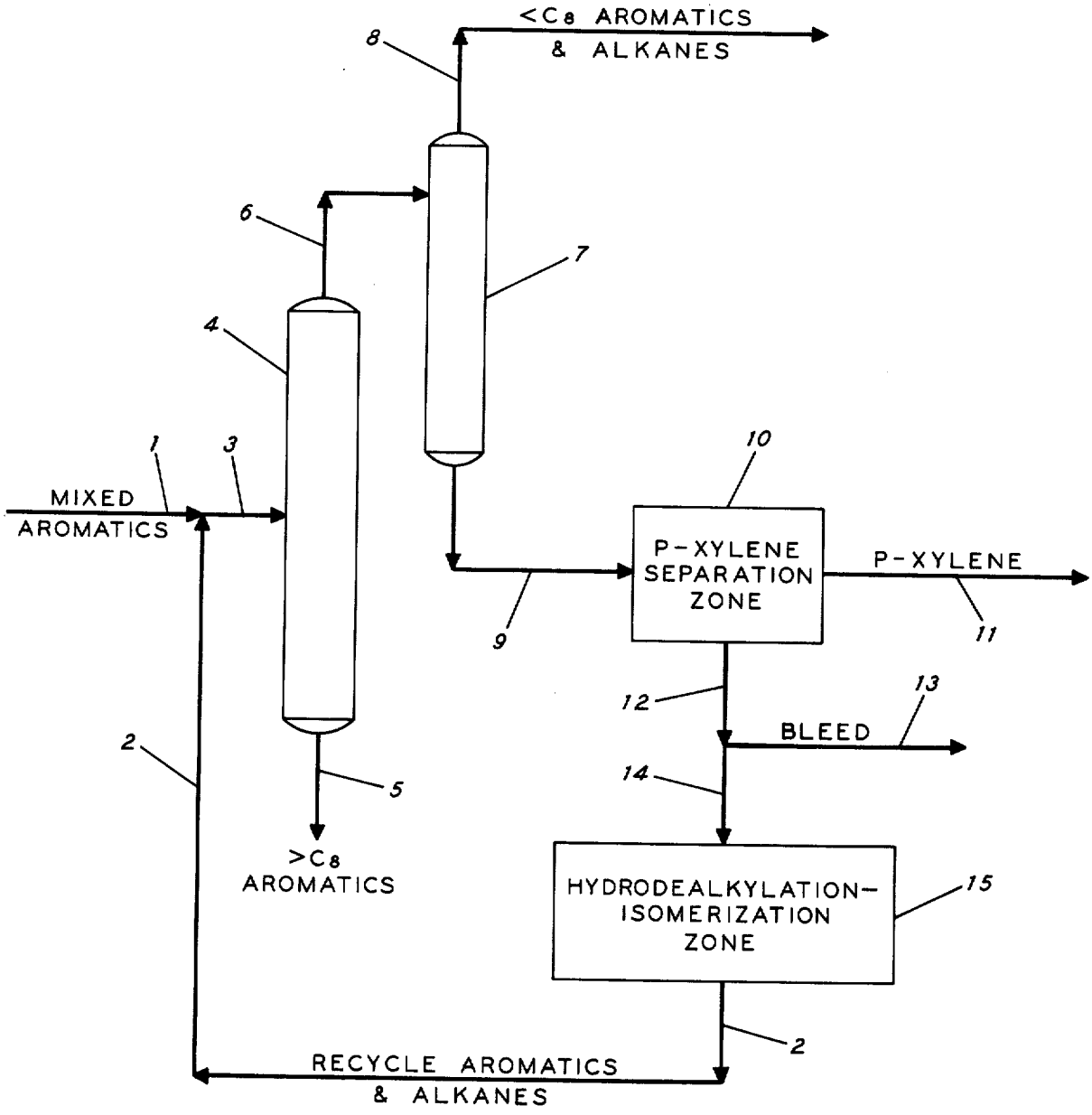
Primary Examiner—Delbert E. Gantz
Assistant Examiner—C. E. Spresser
Attorney, Agent, or Firm—G. F. Magdeburger; John Stoner, Jr.; T. G. De Jonghe

[57] **ABSTRACT**

A process for selective hydrodealkylation of ethylbenzene in a hydrocarbon feedstock comprising ethylbenzene and xylenes, and for simultaneous isomerization of the xylenes, which comprises contacting the feedstock with a catalyst comprising a cobalt or nickel component on an acidic inorganic refractory oxide support at a temperature between 650°–950°F., a pressure below 300 psig, and a hydrogen-to-hydrocarbon feed ratio between 1:1 and 20:1. Preferably the catalyst used is cobalt on silica-alumina.

3 Claims, 1 Drawing Figure




<C8 AROMATICS
& ALKANES
8
6
7
4
1
3
MIXED
AROMATICS
10
P-XYLENE
SEPARATION
ZONE
P-XYLENE
9
11
12
13
BLEED
2
5
14
>C8
AROMATICS
HYDRODEALKYLATION-
ISOMERIZATION
ZONE
15
2
RECYCLE AROMATICS
& ALKANES

HYDROGENOLYSIS/ISOMERIZATION PROCESS

BACKGROUND OF THE INVENTION

The present invention relates to concurrent hydrodealkylation and isomerization of alkyl aromatics, preferably hydrodealkylation of ethylbenzene with simultaneous isomerization of xylenes.

Hydrodealkylation of alkyl aromatics has been known for some time. For example, U.S. Pat. No. 2,422,673 discloses hydrodealkylation or demethylation of an alkyl aromatic using a catalyst containing nickel or cobalt on diatomaceous earth. Temperatures used in the process of U.S. Pat. No. 2,422,763 are between 350°–650°F. and pressures are between subatmospheric to 1,000 psig. According to the patent, it is generally advisable to carry out the reaction at a fairly low pressure of hydrogen so as to obtain a relatively high proportion of demethylation and a relatively small amount of hydrogenation of aromatic hydrocarbons to naphthenic hydrocarbons.

U.S. Pat. No. 2,734,929 also discloses hydrodealkylation of alkyl aromatics, including a process for removing ring-bonded methyl groups from the aromatic ring, which methyl groups are more difficult to remove than splitting a longer-chained alkyl group down to a shorter side-chained group. According to the patent, the catalyst used contains a Group VI-B or Group VIII metal hydrogenation component, such as chromium, molybdenum, tungsten, uranium, iron, cobalt, ruthenium, rhodium, palladium, osmium, iridium or platinum, platinum being the least preferred. The hydrogenation catalyst is preferably suspended on a carrier such as alumina, silica gel, zirconia, thoria, magnesia, titania, montmorillonite clay, bauxite, diatomaceous earth or crushed porcelain. The alumina carrier can also contain some silica. The U.S. Pat. No. 2,734,929 patent discloses preferred operating conditions including a pressure between 150–200 psig and a temperature between 900°–1200°F.

U.S. Pat. No. 3,478,120 discloses a process for hydrodealkylation of ethylbenzene to toluene, benzene, methane and ethane, with the hydrodealkylation being carried out in the presence of xylenes. The catalyst used in the process of U.S. Pat. No. 3,478,120 comprises an iron-group metal on calcium aluminate. Operating conditions include a reaction temperature of about 700°F. and a pressure of about 200 psig.

Isomerization of alkyl aromatics is disclosed in numerous references. For example, U.S. Pat. No. 2,403,757 is an early patent disclosing the use of a synthetic silica-alumina catalyst for xylene isomerization at a temperature between 500°–1100°F. The use of hydrogen or steam in the isomerization of alkyl aromatics is disclosed in U.S. Pat. Nos. 2,564,388, 2,775,628 and subsequent references.

Catalysts with Group VI-B or Group VIII metals supported on a carrier have also been disclosed for hydroisomerization. For example, U.S. Pat. No. 3,113,979 discloses use of a catalyst containing a Group VIII metal such as platinum, as well as boria, on a support such as alumina. U.S. Pat. No. 3,538,174 discloses platinum and iridium on a porous inorganic oxide support as an alkyl-aromatic hydroisomerization catalyst, and also mentions that catalysts such as nickel sulfide on silica-alumina have been proposed as xylene isomerization catalysts. U.S. Pat. No. 3,562,342 discloses hydroisomerization using a catalyst containing nickel and tungsten on a cracking component composed of a mixture of amorphous inorganic oxides and a synthetic crystalline zeolite in hydrogen form. U.S. Pat. No. 3,119,886 discloses hydroisomerization of xylenes using a catalyst containing nickel and tungsten on a synthetic aluminosilicate support.

Isomerization and disproportionation of alkyl aromatics is disclosed in U.S. Pat. Nos. 3,651,162 and 3,578,723. According to U.S. Pat. No. 3,651,162, alkyl aromatic hydrocarbons are isomerized and disproportionated by contacting them at elevated temperatures in the presence of hydrogen gas with a catalyst comprising a silica-alumina cracking base impregnated with a hydrogenation component, a second metal from Group V-A of the periodic table, and a halogen. The preferred hydrogenation component is nickel, the preferred Group V-A metal is arsenic, and the preferred halogen is fluorine. Example 1 of U.S. Pat. No. 3,651,162 discloses conversion of metaxylene to other xylenes, toluene, trimethylbenzene and benzene at a temperature preferably between 700°–900°F.

U.S. Pat. No. 3,578,723 describes the use of a zeolite catalyst for conversion of mixtures such as toluene and trimethylbenzene to xylenes or converting orthoxylene to tri- and tetramethylbenzenes such as durene.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for selectively hydrodealkylating ethylbenzene in a hydrocarbon feedstock comprising ethylbenzene and xylenes, and for simultaneously isomerizing the xylenes, which process comprises contacting the feedstock with a catalyst comprising a cobalt or nickel component on an acidic inorganic refractory oxide support at a temperature between 650°–950°F., a pressure below 300 psig and a hydrogen-to-hydrocarbon feed ratio between 1:1 and 20:1.

I have found that cobalt on silica-alumina is an especially preferred catalyst for use in the process of the present invention.

The cobalt or nickel catalyst components can be present in compound form such as the oxides or sulfides or in elemental form or partly in compound form and partly in elemental form. Preferably the metal is present in the catalyst in a reduced state. Preferably the catalyst is obtained by impregnating a cobalt salt into the support, calcining, and then heating in a hydrogen atmosphere, which results in conversion of a substantial portion of the metal salt into the elemental form. Furthermore, in the presence of hydrogen, as used in the process of the present invention, the cobalt or nickel remains essentially in the elemental form.

Among other factors, the present invention is based on my finding that a high degree of selective hydrodealkylation of ethylbenzene to toluene and benzene can be obtained in the presence of xylenes while simultaneously isomerizing the xylenes, when using a catalyst comprising cobalt or nickel on an acidic inorganic refractory oxide support.

The term "acidic" inorganic refractory oxide support is used herein to connote acid-acting solid supports such as silica-alumina or inorganic refractory oxides such as alumina containing about 0.3 to 5 weight percent halide, namely chloride, bromide or fluoride. Usually a pure alumina support is not sufficiently acidic for purposes of the present invention.

The cobalt or nickel component of the catalyst may be referred to as a hydrogenation component. In accor-

dance with a preferred embodiment of the present invention, the hydrogenation component is cobalt. I have found that a particularly preferred catalyst for use in the process of the present invention comprises a cobalt component on silica-alumina.

Among other factors, this particularly preferred embodiment is based on my unexpected finding that cobalt on silica-alumina is considerably superior to nickel on silica-alumina in terms of the beneficial results achieved in the process of the present invention, including a higher selectivity for ethylbenzene conversion in the presence of xylenes and lower disproportionation losses, than is achieved using the corresponding nickel-containing catalyst.

Preferred operating conditions for use in the present invention include a temperature between 700°–900°F. and a hydrogen pressure between 10–200 psig. Particularly preferred operating conditions, especially when using the cobalt-on-silica-alumina catalyst, include a temperature between 750°–850°F. and a pressure between 10–200 psig. These preferred operating temperatures and pressures are especially important in achieving the simultaneous selective hydrodealkylation of ethylbenzene and isomerization of xylenes.

Preferred hydrogen-to-hydrocarbon ratios for the feed to the process of the present invention are between about 1 to 20, and more preferred ratios are between about 5 to 10.

Preferred space velocities for the hydrocarbon feed to the catalytic reaction zone of the present invention are between about 0.1 to 10 LHSV (liquid hourly space velocity), and more preferably between about 0.3 and 1.0 LHSV.

The present invention has been found to be especially advantageously applied to feedstocks containing a relatively large amount of xylenes, that is, at least 50 weight percent xylenes, and more preferably at least 60 or even as high as 70 or 80 weight percent xylenes. Even though there are large amounts of xylenes present, a selective hydrodealkylation of ethylbenzene has still been found to be achieved when using the process of the present invention. The amount of ethylbenzene in the feed to the present invention is usually between 5 to 40 weight percent, and preferred feedstocks include those having between 10 to 30 weight percent ethylbenzene. With the process of the present invention in operation and with recycle through a paraxylene plant, the ethylbenzene concentration levels out at about **10%**.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic process flow diagram illustrating a preferred embodiment of the present invention.

FURTHER DESCRIPTION AND EXAMPLES

The process of the present invention is useful in refinery operations wherein a C_8 aromatics stream is processed to recover the maximum amount of paraxylene. The paraxylene-reduced effluent from a paraxylene plant is a particularly preferred feedstock in the process of the present invention. Concurrent hydrodealkylation and isomerization prevents the buildup of large quantities of ethylbenzene in the recycle stream, and at the same time converts ortho- and metaxylenes into the more desirable paraxylene. A typical cyclic process utilizing the process of the present invention is shown in the drawing.

As indicated in the drawing, a mixed aromatic feed in line **1**, previously treated to remove nonaromatic components, is combined with the line **2** effluent stream from hydrodealkylation/isomerization plant **15**, fed via line **3** to column **4**, and distilled. The higher-boiling aromatics — those having more than 8 carbon atoms — are taken as a bottoms fraction in line **5**; the overhead is charged via line **6** to another distillation unit, **7**. In this second distillation, the lower-boiling aromatics — those having less than 8 carbon atoms — and the alkanes, methane and ethane are taken overhead in line **8**. The bottoms from the second distillation are then fed via line **9** to paraxylene plant **10**, wherein about 25 to 95 percent of the paraxylene is removed by crystallization or by extraction, and paraxylene is withdrawn via line **11**. The effluent (mother liquor) from the paraxylene plant then is withdrawn via line **12** and is fed to the concurrent hydrodealkylation/isomerization plant **15**. Provision is made via line **13** to bleed some of the paraxylene plant mother liquor as desired. Finally, the ethylbenzene-reduced/xylene-isomerized stream from the hydrodealkylation/isomerization plant is recycled to be combined with incoming fresh feed.

Typical fresh feed to such a combined process contains about 15 to 30 percent ethylbenzene based on C_8 aromatics. The recycle stream contains about 5 to 15 percent ethylbenzene based on C_8 aromatics. Finally, when operating this above-described combined process in a continuous manner, the quantity of recycle C_8 aromatics is from two to four times that of the fresh feed; and, as a consequence, the ethylbenzene in the feed to the paraxylene plant levels out at less than 10 percent, as compared to about 20 percent on a once-through or single-pass basis. Such a reduction in ethylbenzene concentration increases the efficiency of the paraxylene plant, especially one using crystallization-type separation.

The catalysts used in the process of the present invention are preferably prepared by mixing the desired solid support with an aqueous solution of a cobalt or nickel salt. The resulting slurry can be evaporated to dryness, or the solution-covered solid support can be filtered from the slurry and dried. In the first method, the slurry must be stirred during evaporation to ensure even coverage. In the second method, this is not necessary. In the first method of catalyst preparation, the quantity of metal on the catalyst support is easily controlled.

Cobalt and nickel salts useful in the formation of aqueous solutions for catalyst preparation include the nitrates, acetates and sulfates. The nitrates are preferred.

EXAMPLE 1

Preparation of a cobalt catalyst

A solution of 5.0 g of cobalt nitrate in sufficient water to give 32 ml was added to 95 g of a 90/10 silica/alumina support. The solid material was blotted dry after 15 minutes of immersion. It was then dried in an oven at 250°F. for 16 hours. A portion of this dried material — 27.25 ml — was charged to a ½ inch-diameter stainless-steel tubular reactor. It was then heated at 900°F. in air for one hour at atmospheric pressure and then at 900°F. in a hydrogen atmosphere for one hour at 100 psig. The resulting catalyst contained 1.3 percent by weight of cobalt.

EXAMPLE 2

Preparation of a nickel catalyst

The procedure of Example 1 was followed, except that the impregnating solution contained 12.3 g of nickelous nitrate in sufficient water to give 35.2 ml. The resulting catalyst contained 2.4 percent nickel.

EXAMPLES 3–8

Other catalysts

Other catalysts were prepared in a similar way to give a range of metal concentrations and to give a variety of supports. These were as follows:

Example	Support	Metal	Percent Metal
3	Alumina	Cobalt	11.0
4	Silica	Cobalt	5
5	Silica/Alumina	Cobalt	6.5
6	Silica/Alumina	Cobalt	3.4
7	Silica/Alumina	Nickel	1.1
8	Silica/Alumina	None	0

EXAMPLE 9

Hydrodealkylation/Isomerization

(a) A stainless-steel, vertical, tubular reactor, having an ID of ½ inch and mounted in an electrically heated metal block, was charged with the catalyst of Example 5. The reactor was heated to 800°F., and the pressure was adjusted to 75 psig. Then hydrogen and a C_8 aromatic hydrocarbon in a molar ratio of 7.6:1 was fed to the reactor at an LHSV of 0.88 hr^{-1}. The aromatic hydrocarbon contained 23% ethylbenzene, 8.1% paraxylene, and 66.5% other xylenes. After 16 hours on stream, the effluent hydrocarbon was analyzed by mass spectra and vapor-phase chromatography and found to contain the following components (in weight percent): 0.7% nonaromatics, 0.7% benzene, 12.2% toluene, 11.5% ethylbenzene, 14.4% paraxylene, 38.7% metaxylene, 19.7% orthoxylene, and 2.2% C_9+ aromatics. Thus, the reaction hydrodealkylated 50 percent of the ethylbenzene (11.5/23 × 100) and concurrently isomerized the xylenes to increase the quantity of paraxylene with only a 2.4 percent loss in total xylenes. The isomerization level of the product was 84.9 percent, compared to 46.8 percent for the feedstock. Isomerization level (IL) refers to the percent approach to xylene equilibrium, and is calculated by the following formula:

$$IL = \frac{\text{Weight paraxylenes}}{\text{Weight total xylenes}} \times \frac{100}{0.232}$$

For commercially useful processes, the IL should be over 80 percent, preferably in the range 90 to 100 percent.

b. The temperature was then raised to 875°F., and the run was continued for 8 more hours. At the end of this time, the product stream had an IL of 92.2 percent, and 71.3 percent of the ethylbenzene in the feed was removed by hydrodealkylation with only an 8.6 percent loss of total xylenes. The ratio of ethylbenzene loss to xylene loss is 8.3 (71.3/8.6).

This example shows that concurrent hydrodealkylation and xylene isomerization take place over the catalyst of this invention and that the levels of both are increased by increasing the temperature. Furthermore, it shows that these beneficial results are obtained without an uneconomical loss of xylenes.

EXAMPLE 10

No metal on the support

The reactor of Example 9 was charged with the catalyst of Example 8. Hydrogen and an aromatic feed having 21.5% ethylbenzene, 10.1% paraxylene and 68.4% other xylenes were fed to this reactor at an LHSV of 0.44 hr^{-1}. The mol ratio of hydrogen/hydrocarbon was 5.0:1. The reactor was maintained at a temperature of 800°F. and a pressure of 50 psig. Under these conditions, the product stream had an isomerization level of 98.1 percent, but the hydrodealkylation of ethylbenzene was very low — about 15 percent. Xylene loss was 9.2 percent.

This example illustrates that the silica/alumina support without metal effects isomerization but is a poor hydrodealkylation catalyst and is essentially nonselective in hydrodealkylation; the ethylbenzene loss/xylene loss ratio was only 1.5.

EXAMPLE 11

Cobalt on an alumina support & on a silica support

a. The catalyst of Example 3 was charged to the same reactor as in the previous examples and was then heated to 825°F. Hydrogen and an aromatic feed having 26.3% ethylbenzene, 9.4% paraxylene, and 59.5% other xylenes were charged at an LHSV of 2.4 hr^{-1}. The hydrogen/aromatic hydrocarbon mol ratio was 4.8:1. The pressure was 215 psig. The product stream had an IL of 58.6 percent. Ethylbenzene loss by hydrodealkylation was 60.9 percent, and xylene loss was 21.5 percent.

b. The same run was carried out over the catalyst of Example 4, except that the pressure was 205 psig and the temperature was 775°F. In this case, the product had an IL of 56.9 percent and an ethylbenzene hydrodealkylation loss of 56.3 percent. The xylene loss was 10.5 percent.

The two runs of this example illustrate that the metal portion of the catalyst on either an alumina or a silica support alone effects hydrodealkylation of ethylbenzene without any isomerization of xylenes (IL of feedstock 58.5 percent).

EXAMPLE 12

Comparison of cobalt and nickel catalysts

a. The catalyst of Example 1 was charged to the reactor and heated to 800°F. under a pressure of 100 psig. Then hydrogen and an aromatic hydrocarbon in a molar ratio of 10.4:1 was fed at an LHSV of 0.73 hr^{-1}. The aromatic feed contained 9.7% ethylbenzene, 9.9% paraxylene, and 80.4% other xylenes. The product had an IL of 94.4 percent. The hydrodealkylation of ethylbenzene was 16.6 percent, and the xylene loss was 5.7%.

b. The catalyst of Example 2 was then charged and heated to 800°F. under a pressure of 80 psig. Hydrogen and an aromatic hydrocarbon in a molar ratio of 4.9:1 were fed at 0.73 hr^{-1}. This aromatic feed contained 8.5% ethylbenzene, 9.2% paraxylene, and 91.3 percent other xylenes. The product from this reaction had a 94.8% IL, and the hydrodealkylation of ethylbenzene

was 76.5 percent. However, the hydrodealkylation loss of xylenes was 28.5 percent.

These two runs illustrate the superiority of cobalt over nickel as the metallic portion of the catalysts used in the process of the present invention. Both metals effect about the same level of isomerization, but under conditions that give a nickel catalyst this degree of activity, too much xylene is lost to hydrodealkylation. Lowering the temperature in run **12**(b) to 750°F. did lower the xylene loss to 20.3 percent, but at the same time the IL dropped to 87.9 percent. At the commercially feasible 10 percent or less xylene hydrodealkylation loss, the IL is well below the feasible level.

c. Another run was carried out using the nickel catalyst of Example 7 under similar conditions — i.e., 800°F., 80 psig, 0.73 hr^{-1} LHSV, and a **4.9:1** ratio of reactants. The IL was 98.3 percent, but at the same time 22.8 percent of the xylenes were lost.

d. Another run was carried out using the cobalt catalyst of Example 1 under more strenuous conditions than in any of Example **12**(a), (b) or (c) — i.e., 900°F., 83 psig, 0.44 hr^{-1} LHSV, and a molar ratio of reactants of **3.4:1.** In this case, the IL was 97.2 percent, but the loss of xylenes was only 6.3 percent, and hydrodealkylation removed 19.7 percent of the ethylbenzene.

This last run illustrates the specificity and superiority of the cobalt catalyst to effect a high degree of isomerization without a correspondingly high loss of xylenes to other aromatic by-products.

EXAMPLE 13

A low-pressure reaction

The catalyst of Example 4 was charged to the reactor and heated to 800°F. under 14 psig. Then hydrogen and an aromatic feedstock in a molar ratio of 4.9:1 was fed at an LHSV of 0.37 hr^{-1}. The aromatic feed contained 9.2 percent ethylbenzene, 10.7 percent paraxylene, and 80.1 percent other xylenes. The product had an IL of 97.5 percent. Hydrodealkylation of ethylbenzene was 34.5 percent, and loss of xylene was 8.9 percent.

What is claimed is:

1. A process for selective hydrodealkylation of ethylbenzene in a hydrocarbon feedstock comprising ethylbenzene and xylenes, to thereby convert ethylbenzene to toluene and benzene, and for simultaneous isomerization of the xylenes, which comprises contacting the feedstock with a catalyst consisting essentially of a cobalt component on a silica-alumina support at a temperature between 650° and 950°F., a pressure below 300 psig, and a hydrogen-to-hydrocarbon feed ratio between 1:1 and 20:1.

2. A process in accordance with claim **1** wherein the temperature is between 700°–900°F. and the pressure is between 10 psig and 200 psig.

3. A process in accordance with claim **1** wherein the temperature is between 750°–900°F. and the pressure between 10 psig and 200 psig.

* * * * *