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PROCESS FOR THE AROMATIZATION OF HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

Aromatization of hydrocarbons, such as straight-run gasoline fractions, is effected by passing the hydrocarbons at a temperature of 400–550° C. and a pressure of up to 20 atm. over a platinum alumina catalyst containing 0.1 to 5% by weight of palladium and 0.1 to 5% by weight of at least one element from the scandium subgroup of Group III or the zirconium subgroup of Group IV of the Periodic Table of Elements. A mixture of an element from the scandium sub group and of the zirconium subgroup is particularly effective, e.g. cerium and zirconium.

This invention relates to processes for the aromatization of hydrocarbons over platinum alumina catalysts.

A previously known process for the aromatization of hydrocarbons comprises the catalytic reforming of straight-run petroleum fractions over a platinum alumina-catalyst under a pressure of not less than 20 atm. and at a temperature of 475–520° C.

In these conditions aromatic hydrocarbons are predominantly formed through the dehydrogenation and dehydroisomerization of naphthenic compounds. In addition there takes place simultaneously dehydrocyclization of n-paraffins, whereby an additional amount of aromatic hydrocarbons is formed. However, the high pressure employed in said catalytic reforming process suppresses the dehydrocyclization of n-paraffins and the greater part of the n-paraffins remains unconverted. Although lowering the pressure substantially increases the yield of benzene by involving n-paraffins in the process, prolonged operation under these conditions is impossible since the catalyst becomes coked and its activity falls sharply in a few score hours. Consequently catalytic reforming is preferably confined to processing gasoline fractions with a high content of naphthenic hydrocarbons. Nevertheless, even in this case the efficiency of the process is far from maximum, inasmuch as the paraffins contained in said fractions are practically not converted into aromatic hydrocarbons. When it comes to petroleum fractions containing a large amount of n-paraffins, processing said fractions over a platinum alumina-catalyst is ineffective in cataytic reforming conditions (20–40 atm. at 475–520° C.), and impossible at a lower pressure.

Consequently, the principal disadvantage of the previously known process for the aromatization of hydrocarbons and the production of benzene by the catalytic reforming of straight-run petroleum fractions is its low efficiency when fractions with a high content of n-paraffins are processed.

Another disadvantage of the catalytic reforming process is that small amounts of chlorine-containing organic compounds are added to the charge in order to maintain high activity of the catalyst. This leads to certain difficulties connected with requiring corrosion-resistant equipment.

In U.S. Pat. 2,814,599 a process for catalytic reforming over a platinum alumina catalyst promoted by an element of the III group of the Periodic system is described. As an example illustrating the advantage of the described catalysts the use of a platinum-alumina catalyst containing gallium for increasing the octane number of benzene is cited in said patent. The product obtained in the presence of the promoted catalyst had an octane number 8 points higher than that of the product obtained when the standard catalyst was employed. Nevertheless improving the quality of the basic product by employing a promoted catalyst is accompanied by a 3-fold increase in the formation of polymeric by-products, which inevitably leads to poisoning of the catalyst and lowering of its activity, and finally to a sharp reduction in its operating life as compared with the standard catalyst. The increase of the octane number of the product obtained by employing the promoted catalyst can be observed only when the compared catalysts are operated for a short period of time (in the example cited in the above U.S. patent the duration of the test was only 8 hours).

It is an object of the present invention to provide a process for the aromatization of hydrocarbons under a low gauge pressure giving a high yield of aromatic hydrocarbons.

It is another object of the invention to provide high activity of the catalyst over a prolonged period of time.

It is still another object of the invention to provide process for the aromatization of n-paraffins giving a high yield of aromatic hydrocarbons over a prolonged period of time.

We have found that these and other objects have been accomplished if the aromatization of hydrocarbons is carried out at atmospheric pressure or under a pressure of not more than 20 atm. and at a temperature of 400–550° C. over a platinum alumina-catalyst containing as additives palladium and an element of the scandium subgroup of the III group of the Periodic system or palladium and an element of the zirconium subgroup of the IV group of the Periodic system, or palladium in combination with elements of both said subgroups. Said additives are contained in the catalyst in the amount of 0.1 to 5 wt. percent each, on the basis of metal.

Although the process for the aromatization of hydrocarbons over the above catalysts gives a good yield at a temperature of 450–550° C. and pressure from atmospheric to 20 atm., the process is preferably carried out at a temperature of 500–550° C. and a pressure from 5 to 15 atm. from the standpoint of the equipment design.

At atmospheric pressure and a temperature of 545° C. the initial yield of benzene from the aromatization of n-hexane reaches 45 wt. percent, the activity of the catalyst falling but slightly over a prolonged period of time. After the passage of 180 equal portions of the feed-stock the yield of benzene is approx. 40 wt. percent. For comparison it can be pointed out that when n-hexane is aromatized at the same conditions over platinum-alumina catalyst without said additives, the initial yield is 39–40 wt. percent, but after the passage of 20 equal portions of the feed-stock the yield falls to 20–22 wt. percent due to catalyst coking.

When a straight-run petroleum fraction containing 73.7% of paraffins is aromatized by the present process over a platinum-alumina catalyst with the addition of palladium and cerium, the initial yield of benzene is 27 wt. percent, and after 200 hours of continuous operation it falls only to 26%, whereas without said additives the yield of benzene over a period of 30 hours falls from 27 to 25 wt. percent and in 50 hours falls to 23.7 wt. percent due to the catalyst coking. The yield of coke per feed-stock unit in the presence of said promoted catalysts is 5 times less than that in the presence of a catalyst without said additives (promoters). High yields are obtained in

the aromatization of n-hexane in the presence of a platinum-alumina catalyst containing 0.6 wt. percent platinum with the addition of 0.5–1.0 wt. percent palladium and 1.5–3 wt. percent cerium, scandium or zirconium, or palladium mixed with said promoters.

In the aromatization of straight-run paraffin-containing gasoline fractions, the best results are achieved when a platinum-alumina catalyst containing an addition of up to 1 wt. percent palladium in combination with 1.5 wt. percent cerium or zirconium is employed.

The present method makes it possible to obtain aromatic hydrocarbons from paraffin-containing gasoline fractions and from paraffins in high yield (26–45 wt. percent, depending on process conditions) without significant lowering of catalyst activity over a prolonged period of time.

The invention will now be described in detail in the following examples.

EXAMPLE 1

Aromatization of n-hexane is carried out at a temperature of 545° C. and atmospheric pressure over a catalyst containing 0.6 wt. percent platinum, 0.2 wt. percent palladium and 1.5% wt. zirconium deposited on aluminum oxide. The specific surface of the carrier is 130 $m.^2$ per g., and the bulk weight 0.6 g. per ml. Impurity content: 0.02 wt. percent sodium and 0.03 wt. percent iron. Catalyst charge, 100 mg. in the form of 0.5–1 mm. granules.

The catalyst is first activized by calcinating in air at 500–550° C. for two hours.

The reaction is carried out in a microapparatus, the raw material being passed through periodically in equal portions of 0.035 ml. Reaction products are analyzed by the gas-liquid chromatographic method.

After the passage of 60 portions of raw material the yield of benzene falls from 45 to 431%.

EXAMPLE 2

Aromatization of n-hexane is carried out in the conditions of Example 1 over a catalyst containing 0.6 wt. percent platinum, 0.5 wt. percent palladium, and 3.0 wt. percent scandium on aluminum oxide.

After the passage of 200 portions of raw material the yield of benzene diminishes from 43–45 to 38–42%, that is, remains practically unchanged.

EXAMPLE 3

Aromatization of n-hexane is carried out in the conditions of Example 1 over a catalyst containing 0.6 wt. percent platinum, 1.0 wt. percent palladium and 1.5 wt. percent cerium on aluminum oxide.

After the passage of 180 portions of raw material the yield of benzene diminishes from 45–46% to 39–43%, that is, very slightly.

EXAMPLE 4

Aromatization of n-hexane is carried out in the conditions of Example 1 over a catalyst containing 0.6 wt. percent platinum, 0.5 wt. percent palladium, 1 wt. percent cerium and 1 wt. percent zirconium on aluminum oxide.

After the passage of 180 portions of raw material the yield of benzene diminishes from 43–45% to 38–40%.

EXAMPLE 5

Aromatization of n-hexane is carried out in the conditions of Example 1 over a catalyst containing 0.6 wt. percent platinum and 0.2 wt. percent palladium on aluminum oxide and in the second variation over a catalyst containing 0.6 wt. percent platinum and 1 wt. percent palladium on aluminum oxide.

After the passage of 20 portions of raw material the yield of benzene drops from 40 to 28%, while in the second variation it diminishes from 40 to 37% after the passage of 20 portions of raw material and to 31% after the passage of 60 portions.

EXAMPLE 6

Aromatization of n-hexane is carried out in the conditions of Example 1 over a catalyst containing 0.6 wt. percent platinum and 1.5 wt. percent zirconium on aluminum oxide.

After the passage of 20 portions of raw material the yield of benzene drops from 37% to 22.5%.

EXAMPLE 7

Aromatization of n-hexane is carried out in the conditions of Example 1 over a catalyst containing 0.6 wt. percent platinum (0.8 wt. percent in the second variation) on aluminum oxide.

After the passage of 20 portions of raw material the yield of benzene drops from 39 to 22% (in the second variation from 40 to 20%).

It is evident from the foregoing examples that the highest yield of benzene during the operation is obtained when an aluminum oxide-base catalyst is employed which contains 0.6 wt. percent platinum, 0.5–1 wt. percent palladium and 1.5–3 wt. percent of elements of the scandium subgroup of the III group and/or elements of the zirconium subgroup of the IV group of the periodic system.

The addition of zirconium alone to the catalyst gives results practically coinciding with those obtained with the usual platinum-alumina catalyst (cf. Examples 6 and 7).

The addition of palladium has a partial effect (cf. Example 5).

Thus, when the catalyst employed contains only 0.2% wt. percent palladium and 1.5 wt. percent zirconium the effect is the same as that obtained when the catalyst contains 1 wt. percent palladium without zirconium.

The results of the foregoing examples are summarized in Table 1.

EXAMPLE 8

Aromatization of a fraction boiling in the range of 62–85° C. is carried out in the presence of the catalyst employed in Example 1 (0.6 wt. percent platinum, 0.2 wt. percent palladium and 1.5 wt. percent zirconium) in the following conditions:

Temperature: 500° C.
Pressure: 5 gauge atm.
Volume feed rate of raw material: 1 $hr.^{-1}$
Circulation of hydrogen containing gas: 1600 $m.^3$ NTP/$m.^3$ raw material
Characteristics of raw material, wt. percent—
Isohexanes: 23.7
n-Hexane: 50.0
Methylcyclopentane: 14.8
Cyclohexane: 6.8
Benzene: 4.7
Sulphur content: 0.0005

After 150 hrs. operation the benzene yield diminishes from 27.4 to 26.2 wt. percent. Coke yield, 0.015 wt. percent (on the basis of the raw material).

EXAMPLE 9

Aromatization of the 62–85° C. fraction is carried out in the conditions of Example 8 in the presence of the catalyst employed in Example 3. After 200 hours operation the benzene yield diminishes from 27.0 to 26.0 wt. percent. Coke yield, 0.01 wt. percent on the basis of the raw material.

EXAMPLE 10

Aromatization of the 62–85° C. fraction is carried out in the presence of an unpromoted platinum-alumina catalyst containing 0.6 wt. percent platinum (catalyst of Example 7). After 50 hours operation the benzene yield falls from 27.0 to 23.7 wt. percent. Coke yield, 0.05 wt. percent on the basis of the raw material.

The results obtained in Examples 8–10 are given in Table 2. It follows from the table that in the presence of promoted catalyst aromatization proceeds without significant reduction in the yield of benzene over a period of 150–200 hours, whereas in the presence of an unpromoted catalyst the benzene yield falls by more than 3% in 50 hours.

EXAMPLE 11

Aromatization on the hexane fraction boiling in the range of 62–85° C. (characteristics of the raw material given in Example 8) is carried out in the following conditions:

Temperature: 500° C.
Pressure: 10 atm.
Volume feed rate of raw material: 1.0 hr.$^{-1}$
Circulation of gas: 200 m.^{3} NTP/m.^{3} raw material

Aromatization is carried out over the catalyst of Example 1. During 100 hours operation the average benzene yield is 26.0 wt. percent.

EXAMPLE 12

Aromatization of the hexane fraction boiling in the range of 62–85° C. is carried out in the conditions of Example 11, in the presence of the catalyst of Example 3. During 300 hours operation the average benzene yield is 26.0 wt. percent.

EXAMPLE 13

Aromatization of the hexane fraction boiling in the range of 62–85° C. is carried out in the presence of the unpromoted catalyst of Example 7 containing 0.6 wt. percent platinum. During 100 hours operation the average benzene yield is 20%.

EXAMPLE 14

Aromatization of a hexane-heptane fraction boiling in the range of 62–105° C. is carried out in the presence of the catalyst of Example 3 in the following conditions:

Temperature: 500° C.
Pressure: 20 atm.
Volume feed rate of raw material: 1.5 hr.$^{-1}$
Gas circulation: 1200 m.^{3} NTP/m.^{3}
Characteristics of raw material, wt. percent—
Fraction 62° C.: 17
Fraction 62–85° C.: 37
Fraction 85° C.: 46
Group composition—
Paraffin hydrocarbons: 68
Naphthenic hydrocarbons: 28
Aromatic hydrocarbons: 4

During 300 hours operation the average yield of aromatic hydrocarbons is 27.0 wt. percent, of the following composition, wt. percent:

Benzene: 9.6
Toluene: 16.0
Xylenes: 1.4

The results obtained in Examples 11–14 are given in Table 3.

TABLE 1.—AROMATIZATION OF n-HEXANE

Catalyst composition, wt. percent			Benzene yield, wt. percent									
Platinum	Palladium	Elements of III-IV groups	1*	20*	40*	60*	80*	100*	120*	140*	160*	180*	200*
0.6	0.2	1.5 zirconium	45	37	35	31							
0.6	0.5	3.0 scandium	43	45	45	44	43	40	40	39	38	42.5	38
0.6	1.0	1.5 cerium	45	45	46	46	44.5	45	42.5	39	43	41	
0.6	0.5	1.0 cerium plus 1.0 zirconium	44	43	45	42	42	43	38.5	38.5	40	40	
0.6	0.2		40	28									
0.6	1.0		40	37	35	31							
0.6		1.5 zirconium	37	25.5									
0.6			39	22									
0.8			40	20									

* Number of portions of raw material.

TABLE 2.—AROMATIZATION OF 62–85° C. FRACTION

Example No.	Catalyst composition, wt. percent			Benzene yield, wt. percent						Coke yield, raw material basis, wt. percent
	Platinum	Palladium	Elements of III-IV groups	15*	30*	50*	100*	150*	200*	
8	0.6	0.2	1.5 zirconium	27.4		26.0	26.5	26.2		0.015
9	0.6	1.0	1.5 cerium	27	27	27	27	26.5	26.0	0.01
10	0.6			27	25	23.7				0.05

* Duration of run in hours.

TABLE 3.—AROMATIZATION OF GASOLINE FRACTIONS

Example No.	Catalyst composition			Process conditions					Yield, wt. percent		
	Platinum	Palladium	Element III-IV groups	Temp., ° C.	Pressure gauge, atm.	Vol. feed rate, v. hr.$^{-1}$	Gas circulation, m.^{3} gas, STP/m.^{3} raw material	Run, hrs.	Raw material fraction, B.P., ° C.	Benzene	Toluene	Xylenes
11	0.6	0.2	1.5 zirconium	500	10	1.0	2,000	100	62–85	26	2.0	
12	0.6	1.0	1.5 cerium	500	10	1.0	2,000	300	62–85	26	2.2	2.2
13	0.6			500	10	1.0	2,000	100	62–85	20	3.0	
14	0.6	1.0	1.5 cerium	500	20	1.5	1,200	300	62–105	9.6	16.0	1.4

We claim:

1. A process for the aromatization of hydrocarbons which comprises passing said hydrocarbons at a temperature of 400–550° C. and a pressure of up to 20 atm. over a platinum-alumina catalyst containing palladium as a first additive and as a second additive at least one element selected from the group consisting of the scandium subgroup of Group III of the Periodic System and the zirconium subgroup of Group IV of the Periodic System,

each additive being present in an amount of 0.1 to 5% by weight, calculated as the metal.

2. A process as claimed in claim 1 wherein the hydrocarbons are straight-run gasoline fractions boiling in the range of 60 to 105° C.

3. A process as claimed in claim 1 wherein the hydrocarbons are n-paraffins.

4. A process as claimed in claim 3 wherein the hydrocarbon is n-hexane.

5. A process as claimed in claim 3 wherein the second additive is scandium.

6. A process as claimed in claim 1 wherein the second additive is cerium.

7. A process as claimed in claim 1 wherein the second additive is zirconium.

8. A process as claimed in claim 1 wherein the second additive is a mixture of cerium and zirconium.

References Cited

UNITED STATES PATENTS

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HERBERT LEVINE, Primary Examiner

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260—673.5; 252—466 PT

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,694,348 Dated September 26, 1972

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, Example 1, line 1 from bottom, "45 to 431%" should read --45 to 31%--.

Table 3, Example 12, last column (xylenes) "2.2" should be deleted.

Signed and sealed this 7th day of May 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
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