

1

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**METHOD OF PRODUCING BENZENE AND ITS
LOW-MOLECULAR WEIGHT HOMOLOGS**

Gdal Nossionovich Maslyansky, Prospekt Obukhovskoi
Oborony 23, kv. 18; Georgy Lazarevich Rabinovich,
Ulitsa Kibalchicha 16, kv. 34; Nina Khrisanfovna
Avtonomova, Zverinskaya ulitsa 7/9, kv. 48; and Kira
Lvovna Brisker, Naberezhnaya Chernoi Rechki 10,
kv. 30, all of Leningrad, U.S.S.R.

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1 Claim

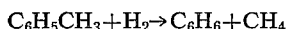
ABSTRACT OF THE DISCLOSURE

Alkyl benzenes are dealkylated with steam at a temperature of 380-600° C. in the presence of a catalyst. The catalyst is a binary system consisting of platinum, palladium, rhodium, irridium, ruthenium or mixtures thereof, deposited in an amount of 0.05 to 5% by weight on a carrier consisting of aluminum oxide, aluminosilicate, a combination of aluminum oxide with oxides of nickel or aluminum oxide with oxides of cobalt.

DETAILED DESCRIPTION

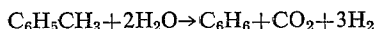
The present invention relates to methods of producing benzene and its low-molecular weight homologs which are used as a raw material for producing diverse synthetic products.

Widely used in industry in the production of benzene are processes consisting in the dealkylation of toluene and other alkyl benzenes, according to the hydrodealkylation reaction:



These processes are carried out in the presence of catalysts or without them at 600-800° C. and at hydrogen pressure of 30-50 atm. A serious disadvantage of these processes lies in the drastic conditions involved and the requirement of large amounts of hydrogen.

There is known in the art a method of producing benzene by the dealkylation of alkyl benzenes by conversion with steam at 350-450° C. in the presence of a nickel-chromium catalyst containing a large amount of nickel (50% Ni). The dealkylation with steam proceeds, according to the reaction:



The disadvantage of this method is the low efficiency of the process. For example, at 375° C. and 0.4 hr.⁻¹ volume rate of the toluene charge, the yield of benzene reaches only 38-39 mole percent based on the toluene passed and reaches 90 mole percent based on converted toluene. When the temperature is raised up to 430° C. the yield of benzene based on toluene passed increases but it is accompanied by a side reaction involving the destruction of the benzene ring, as the result of which the yield of benzene based on the amount of toluene converted decreases to 75-80 mole percent.

Another disadvantage of this method lies in the rapid deactivation and mechanical destruction of the catalyst.

The main object of the present invention is to obtain higher yields of the final product under conditions of dealkylation of alkyl benzenes by conversion with steam.

A further and more specific object of the invention is to provide a catalyst having a long service life.

The above objects are satisfied by the present method of producing benzene and its low-molecular weight homologs by the dealkylation of alkyl benzenes through conversion with steam at a temperature of 380-600° C.,

2

wherein, according to the invention, the catalysts are the noble metals of the VIII Group in the Periodic System: platinum, palladium, rhodium, irridium, ruthenium or their mixtures which are deposited in an amount of 0.05-5% by wt. on a carrier consisting of aluminum oxide, aluminosilicate or the combination of aluminum oxide with oxides of nickel or cobalt.

It is preferable to use a catalyst containing rhodium in the amount of 0.1-1.5% by wt. based on the weight of the carrier, or a mixture of rhodium and platinum or palladium in a weight ratio from 1:5 to 5:1.

As a carrier it is preferable to use the active form of aluminum oxide (γ -Al₂O₃) and a combination of aluminum oxide and oxides of nickel containing from 1 to 40% by wt. of nickel oxides calculated as nickelous oxide.

The combination of aluminum oxide and the oxides of nickel or cobalt can be obtained by impregnating aluminum oxide particles with the solutions of the said metal salts or by precipitating the corresponding hydroxides with aluminum hydroxide. Such a mixed carrier, independent of the method used in obtaining it, must be calcined in an air current at 500-1000° C. until compounds of the spinel type (for example, NiAl₂O₄) are formed, from which compounds the reduction of metals is extremely difficult.

In order to produce benzene, alkyl benzenes of various structures and having various molecular weights preferably toluene and xylenes, are subjected to dealkylation in the presence of steam.

The space velocity of feeding alkyl benzenes lies in the range of 0.2-5 volumes per volume of catalyst per hour. The molar ratio of water: alkyl benzene is kept within the limits of (1-12):1.

In the process are obtained products of complete dealkylation (benzene) and partial dealkylation such as toluene and xylenes. Together with these liquid products are also formed gaseous products containing 40-75 mole percent of hydrogen, 18-30 mole percent of carbon dioxide, 3-40 mole percent of carbon monoxide and methane.

The preparation of the catalyst consists in the treatment of the said carriers with solutions of the compounds of noble metals of the VIII-Group.

To deposit noble metals on the above-mentioned carriers, aqueous solutions of the noble metal compounds are used.

Especially effective are rhodium and mixtures of rhodium with platinum and palladium.

As soluble compounds of rhodium, platinum, and palladium can be used, for example, RhCl₃·3H₂O, H₂PtCl₆·6H₂O, PdCl₂.

Homogeneous impregnation throughout the entire volume of the carrier granules is achieved by adding 0.1-10% of mineral or organic acid (for example, acetic acid) to a solution of noble metal compound (for example, Rh) or a mixture of noble metal compounds (for example, Rh and Pt).

Following the treatment of the carriers with the solutions of the noble metal compounds, the catalysts are dried at room temperature in air for 10-24 hrs.; then the temperature is gradually raised to 130-150° C. during a period of 5-20 hours. After being dried the catalysts based on aluminum oxide or aluminosilicate are calcined in a current of air at 300-600° C. for a period of 0.5-10 hours.

Then the catalysts are treated with hydrogen or hydrogen-containing gas while the temperature is gradually raised to 300-600° C. and maintained at this level for a period of 0.5-24 hours. The hydrogen is fed at a space velocity of 100-2000 l. per liter of the catalyst per hour. The final step consists in the treatment of the catalyst heated to 300-600° C. with steam. Steam is passed

through a catalyst layer at a space velocity of 0.2–5 hr.⁻¹ (calculated as water) for a period of 0.25–10 hours.

The catalyst can be made either in the form of spheres, tablets, or particles of irregular form.

The advantage of the present method of producing benzene and its low-molecular weight homologs is its high efficiency.

Thus with the space velocity of toluene (temperature 430–480° C.) being 0.5 hr.⁻¹ and molar ratio of water: toluene being 4:1, the yield of benzene based on toluene passed reaches 50–65 mole percent, and that based on converted toluene reaches 88–94 mole percent.

Another advantage of the present method lies in the possibility of carrying out the process over an extended period of time without the need for replacing the catalyst.

The present method is carried out under relatively mild conditions, preferably at 430–530° C. and at atmospheric or elevated pressures (not exceeding 50 atm.) and without the use of hydrogen in the process.

(I) In the present process, gas containing from 40 to 75 mole percent of hydrogen is liberated as a by-product.

(II) After being purified from carbon oxides, said gas may be used in the processes of hydrogenation, hydrofining of fuels and oils or in some other processes.

For a better understanding of the present invention the following examples are given illustrating the method of producing benzene and its low-molecular weight homologs.

EXAMPLE 1

Thirty-two g. of γ -Al₂O₃ calcined at 550° C. (dimension of the tablets: length 5 mm., diameter 2.5 mm.) having a bulk weight of 0.56 g./ml. are impregnated with 35 ml. of a solution containing H₂PtCl₆ (0.096 g. Pt) and RhCl₃ (0.096 g. Rh). The catalyst is left in the air for 15 hours and then dried for 3 hours at each of the following temperatures: 50° C., 110° C., 130° C. Then the catalyst is calcined in an air current while being gradually heated to 500° C. and kept at this temperature for 2 hours. The air is fed at a space velocity of 500 volumes per volume of the catalyst per hour. The catalyst is cooled to room temperature, then heated to 500° C. in a current of hydrogen and kept for 2 hours at this temperature. The hydrogen is fed at a space velocity of 500 hr.⁻¹. Then the catalyst is treated for 1 hour with steam at 460° C., the water being delivered at a space velocity of 0.4 hr.⁻¹. The catalyst contains 0.3% Pt and 0.3% Rh based on the weight of Al₂O₃.

The obtained catalyst is tested in a reaction involving the demethylation of toluene by conversion with steam. The amount of the catalyst charged into a tubular reactor is 50 ml. Toluene is delivered at a space velocity of 0.5 hr.⁻¹ (25 ml./hr.); the molar ratio of water: toluene is maintained at 4:1. At the reaction temperature of 460° C. the yield of the liquid product is 85.2% by wt.; the yield of benzene based on toluene passed is 62 mole percent, and that based on converted toluene is 92 mole percent. The composition of the gaseous products is as follows (percent by vol.): H₂—70.0, CO₂—22.5, CO—3.5, CH₄—4.0.

EXAMPLE 2

Thirty-five g. of γ -Al₂O₃ impregnated with 39 ml. of a rhodium chloride solution containing (calculated as metal) 0.21 g. of rhodium. The solution for impregnation also contains 3% acetic acid. The catalyst is dried, calcined in an air current, and treated in a current of hydrogen and steam, as described in Example 1. The catalyst contains 0.6% Rh based on the weight of the said carrier.

The active component (Rh) is homogeneously distributed throughout the entire volume of aluminum oxide granules.

The demethylation of toluene with steam is carried out under conditions as described in Example 1. The yield of the liquid product is 85.7% by wt.; the yield of benzene

based on toluene passed is 54.0 mole percent, and that based on converted toluene is 90 mole percent. The composition of the gaseous products is as follows (percent by vol.): H₂—69.8, CO₂—21.5, CO—4.0, CH₄—4.7.

EXAMPLE 3

Thirty-five g. of γ -Al₂O₃ are impregnated with 39 ml. of a solution containing PdCl₂ and RhCl₃ in amounts equivalent to 0.14 g. of Pd and 0.07 g. of Rh. The catalyst is dried and subjected to treatment as described in Example 1. The catalyst contains 0.4% Pd and 0.2% Rh based on the weight of the carrier. Demethylation of toluene is carried out under conditions as described in Example 1.

The yield of the liquid product is 90.4% by wt.; the yield of benzene based on toluene passed is 49.5 mole percent, and that based on converted toluene is 95.9 mole percent.

The composition of the gaseous products is as follows (percent by vol.): H₂—71.0, CO₂—23.5; CO—3.5; CH₄—2.0.

EXAMPLE 4

One hundred g. of γ -Al₂O₃ are impregnated with 110 ml. of a nickel nitrate solution containing 15 g. Ni (calculated as metal), dried and then calcined for 5 hours in a current of air at 800° C. The obtained aluminonickel carrier has the following composition (wt. percent): NiO—16, Al₂O₃—84. Thirty-five g. of the obtained aluminonickel carrier (bulk weight 0.67 g./ml.) are impregnated with 35 ml. of rhodium chloride solution containing 0.21 g. of rhodium (calculated as metal). The catalyst is dried at a temperature not exceeding 130° C. and then treated in a current of hydrogen for 2 hours at 550° C. Then the catalyst is treated with steam for 1 hour at 430° C., water being fed at a space velocity of 0.5 hr.⁻¹.

The catalyst contains 0.6% Rh based on the weight of the said carrier.

The above-described catalyst is used for an extended run with toluene being fed at a space velocity of 1 hr.⁻¹ and the molar ratio of water: toluene being 4:1, while the temperature is gradually raised from 440° C. to 465° C. within a period of 30 days. The constant yield of benzene per toluene passed is 44–46 mole percent, and that based on the amount of converted toluene is 90 mole percent.

The composition of the gaseous products is as follows (percent by vol.): H₂—72.0, CO₂—22.5, CO—2.5, CH₄—3.5.

EXAMPLE 5

The dealkylation of ortho-xylene is carried out by using a catalyst containing 0.6% Rh (as described in Example 2). At 475° C. with the space velocity of o-xylene feed being 0.5 hr.⁻¹ and the molar ratio of water: o-xylene being 6:1, the yield of the liquid product is 82.4% by wt.; the yield of benzene and toluene based on o-xylene passed is respectively 38.2 mole percent and 30.0 mole percent, while the yield of benzene and toluene based on converted o-xylene is respectively 53.2 mole percent and 41.8 mole percent. The composition of the gaseous products is as follows (percent by vol.): H₂—67.0, CO₂—22.0, CO—6.5, CH₄—4.5.

EXAMPLE 6

The demethylation of toluene with steam is carried out at 460° C. by using a catalyst containing 0.6% by wt. rhodium on an aluminosilicate carrier (80% Al₂O₃), with the molar ratio of water: toluene being 4:1 and toluene being fed at the space velocity of 0.5 hr.⁻¹. The yield of the liquid product is 90.8% by wt.; the yield of benzene based on toluene passed is 38.0 mole percent, and that based on converted toluene is 91.7 mole percent.

The composition of the gaseous products is as follows (percent by vol.): H₂—70.3, CO₂—23.6, CO—2.1, CH₄—4.

5

EXAMPLE 7

The demethylation of toluene with steam is carried out at 470° C. and a pressure of 15 atm. by using a catalyst containing 0.6% Rh on an Al₂O₃ carrier (prepared as described in Example 2). The space velocity of toluene feed is 1 hr.⁻¹, the molar ratio of water: toluene being maintained at 4:1. The yield of the liquid product is 88.2% by wt.; the yield of benzene based on toluene passed is 42.7 mole percent, and that based on converted toluene is 89.4 mole percent. The composition of the gaseous products is as follows (percent by vol.): H₂—45.3, CO₂—28.6, CO—0.6, CH₄—25.5.

What we claim is:

1. A method of producing benzene and its low-molecular weight homologs by dealkylation of alkyl benzenes, preferably toluene and xylenes, said method comprising dealkylating alkyl benzenes with steam at a temperature of 380–600° C. in the presence of a catalyst consisting essentially of noble metals selected from the group con-

6

sisting of platinum, palladium, rhodium, iridium, ruthenium, and their mixtures deposited in the amount of 0.05–5% by weight on a carrier selected from the group consisting of aluminum oxide, aluminosilicate, a combination of aluminum oxide with oxides of nickel and of aluminum oxide with oxides of cobalt.

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15 DELBERT E. GANTZ, Primary Examiner
G. E. SCHMITKONS, Assistant Examiner

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