United States Patent Office 3,002,035 Patented Sept. 26, 1961

3,002,035

PROCESS FOR PREPARING PARA-XYLENE

Ernst Hieronymus, Frankfurt am Main, Germany, assignor to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, Frankfurt am Main, Germany, a corporation of Germany

No Drawing. Filed May 10, 1957, Ser. No. 658,220
Claims priority, application Germany May 16, 1956
4 Claims. (Cl. 260—673.5)

The present invention relates to a process for preparing para-xylene.

It has already been proposed to produce aromatic hydrocarbons from 2.4.4-trimethylpentene and trimethylpentane by passing these hydrocarbons at a raised temperature in the presence or absence of a carrier gas over a known solid catalyst. In this process it is especially useful to use hydrogen and/or isobutylene as a carrier gas. Thus, for example, 2.2.4-trimethylpentane and/or 2.4.4-trimethylpentene-1 and/or 2.4.4-trimethylpentene-2 may be converted to para-xylene. In the aforesaid processes para-xylene is obtained in a proportion of about 10–20% of the resulting liquid products which corresponds in one passage to about 8–15% calculated upon the starting material used. If it was desired to obtain more concentrated products, the proportion of cracking gases would simultaneously be increased so that in this case the total yield would even be reduced.

Now I have found that para-xylene can be obtained in a good yield and in a high concentration of up to about 80% by weight by reacting at a temperature within the range of 450–650° C. diisobutylene (2,4,4-trimethylpentene-1 and/or 2,4,4-trimethylpentene-2), triisobutylene or hydrogenation products or mixtures thereof at a relatively low charge per volume and hour (0.4–0.9 l. of liquid hydrocarbon per liter of contact space and time) in the presence of at least 30% by volume of methane and/or nitrogen as diluting gas, calculated upon the total volume of diluting gas and vaporous hydrocarbon. It is preferred to operate at a temperature within the range of 520–590° C.; the contact time generally is 0.1–60 seconds, advantageously 1–12 seconds.

The yield of para-xylene obtained in the process of this invention depends on the temperature and contact time. The degree of aromatization increases as the temperature increases. The increase in temperature goes parallel with an increased splitting so that less starting material is recovered whereby the yield is decreased as compared with an operation at a lower temperature.

The contact time influences the reaction like the temperature. If the time of dwell of the substance vapor in the contact space is increased at a constant temperature, both the degree of aromatization and splitting is also increased. Splitting increases preponderantly so that the yield in aromatic hydrocarbons and para-xylene in the liquid product is reduced. By increasing the temperature at a shortened time of stay in a manner such that both factors compensate one another with respect to splitting, there is brought about an improved effect of aromatization. The contact time during which a cyclization, isomerization and aromatization take place by dehydrogenation cannot be shortened at will, since with too strong a shortening dehydrogenation does not proceed far enough.

Best results are obtained using 65–80% by volume of methane and/or nitrogen. It is obvious that such diluting gas may also be used in greater amounts but generally this does not result in a special advantage. In the process of this invention the yields increase at a constant charge per volume and time with increased dilution by methane and/or nitrogen. When more than 80% by volume of methane and/or nitrogen are used, the increase in yield

is immaterial and the work up of the reaction products becomes more difficult.

In carrying out the process of this invention there may be used metal oxides of sub-group 6 of the periodic table, if desired in the form of mixed compounds or in admixture with oxides of titanium, zirconium, thorium or vanadium, optionally with the addition of platinum or palladium metal. These oxides may be applied to carriers of oxides of group III of the periodic table and may contain as activator oxides of the alkali metals and/or alkaline earth metals and/or zinc and/or the rare earths. It is however especially suitable to use chromium oxide gamma-aluminum oxide catalysts, and especially those catalysts which additionally contain potassium oxide and cerium oxide, and in which the proportion of chromium oxide, potassium oxide, cerium oxide, and gamma aluminum oxide may vary within the limits of 5–40, 1–10, 0.5–5, and 93.5–45%. Suitable catalysts have been described for example in Patent Number 2,785,209.

As has further been found it is important that the aromatization be carried out with complete exclusion of moisture. If for example a moved catalyst is used which, after having passed the reactor, is allowed to travel successively through a regenerator charged with air and then through a reduction zone charged with hydrogen or another reducing gas, the catalyst adsorbs part of the water formed whereby the aromatization activity of the catalyst is rapidly reduced.

In order to free the catalyst from adhering water vapor, it is therefore suitable to dry said catalyst and this prior to the reaction by conducting a rinsing gas for example nitrogen over it. It is also useful to dry the starting material and the diluting agent. The vaporous starting mixture used in this invention should not contain more than 0.05% by volume of water.

If, for example, 2.2.4-trimethylpentane and/or 2.4.4-trimethylpentene-1 and/or 2.4.4-trimethylpentene-2 are used and, under the conditions described, passed at 550° C. over a catalyst which consists of chromium-III-oxide, potassium oxide and cerium oxide applied to aluminum oxide, and contain 15% of chromium, 1.7% of potassium and 0.6% of cerium, there is obtained a liquid product of about 38% by weight of the starting material used with a para-xylene concentration of about 76% by weight. The yield in one passage has thus been increased to 29% by weight of the quantity used, that is the yield has been doubled as compared with the known process. It is evident that the work up of products containing the desired aromatic hydrocarbon in so high a concentration entails considerable advantages. Thus for example, very pure para-xylene can be recovered immediately by crystallization without previous distillative separation from the liquid products obtained in the aromatization of corresponding hydrocarbons.

The use of mixtures of diisobutylene and triisobutylene and/or the hydrogenation products thereof is especially suitable from an industrial point of view.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

Example 1

A mixture of 51.5 g./h. of diisobutylene and 30.9 normal liters/h. of methane was passed at a temperature of 550° C. over 100 cc. of a catalyst which was prepared in known manner by impregnating gamma-aluminum oxide with a solution of chromic acid, potassium nitrate and cerium nitrate, then calcined for 5 hours at 550° C. and reduced in a hydrogen current, and which contained 14.7% of chromium, 1.73% of potassium and 0.46% of cerium. The proportion of the methane in the vaporous starting mixture accordingly was 75% by volume.

After one hour there were obtained 19.5 grams of a liquid product with a para-xylene concentration of 76%. In one passage the yield in para-xylene amounted to 30.6% of the theory calculated upon the hydrocarbon used. With the use of 33 percent by volume of methane at a constant charge per volume and time, the yield obtained in one passage was 24.3% of the theory.

Example 2

64.3 grams/hour of diisobutylene and 39 normal liters/hour of nitrogen were passed at 550° C. over 100 cc. of the catalyst of Example 1. After one hour there were obtained 29.2 grams of a liquid product with a para-xylene concentration of 65% by weight. The yield in para-xylene in one passage accordingly was 31.2% of the theory.

Example 3

The catalyst used consisted of gamma-aluminum oxide as a carrier and contained 16.6% of chromium and 3.0% of potassium.

(A) A mixture of 51.5 grams/hour of diisobutylene and 30.9 normal liters/hour of methane containing 2% by volume of water vapor was passed at 550° C. over 100 cc. of the above catalyst.

After one hour, there were obtained 22 grams of a liquid product with a para-xylene concentration of 50.5% by weight. The yield in para-xylene in one passage accordingly was 22.8% of the theory.

(B) The conditions were otherwise the same as described sub (A) with the exception however that the content of water vapor in the vaporous starting mixture was less than 0.05% by volume. After one hour, there were obtained 22 grams of a liquid product with a para-xylene concentration of 78% by weight. The yield obtained in one passage was here 35.2% of the theory.

I claim:

1. A process for the manufacture of para-xylene, which comprises aromatizing a compound selected from the group consisting of diisobutylene, triisobutylene, hydrogenation products thereof and mixtures thereof, in the presence of a solid, chromium oxide-containing aromatization catalyst, at a temperature in the range from 450° C. to 650° C. at a charge per volume and time of 0.4 to 0.9 liter of liquid hydrocarbon per liter of contact space and hour in the presence of 65% to 80% by volume of a diluent selected from the group consisting of nitrogen, methane and mixtures thereof, the percentage figure being calculated upon the total volume of the diluent and the vaporized starting material.

2. In a process for the manufacture of p-xylene which comprises aromatizing a hydrocarbon of the group consisting of diisobutylene, triisobutylene, hydrogenation products thereof and mixtures thereof in the presence of a chromium oxide-containing aromatization catalyst at an elevated temperature, the improvement which comprises conducting the aromatization at a charge per volume and time of 0.4 to 0.9 liter of liquid hydrocarbon per liter of contact space and hour, and in the presence of 65 to 80% by volume of a diluent selected from the the group consisting of nitrogen, methane, and mixtures thereof, the percentage being calculated upon the total volume of the diluent and the vaporized starting material.

3. A process for the manufacture of para-xylene which comprises dehydrating a vaporous starting mixture of diisobutylene and triisobutylene with 65 to 80% by volume of a diluent of the group consisting of nitrogen, methane and mixtures thereof, the percentage figures being calculated upon the total volume of the vaporous starting mixture, to a water vapor content of less than 0.05% by volume and aromatizing the diisobutylene and triisobutylene in said dehydrated and vaporous starting mixture in the presence of a solid aromatization catalyst consisting of 5 to 40% of chromium oxide, 0.5 to 5% of cerium oxide, 1 to 10% of potassium oxide and 93.5 to 45% of aluminum oxide, at a temperature in the range from 450 to 650° C., and at a charge per volume and time of 0.4 to 0.9 liter of liquid hydrocarbon per liter of contact space and hour.

4. In a process for the manufacture of para-xylene which comprises aromatizing a starting material of the group consisting of diisobutylene, triisobutylene, hydrogenation products thereof and mixtures thereof in the presence of a chromium oxide-containing aromatization catalyst at an elevated temperature and at a charge rate per volume and time of 0.4 to 0.9 liter of liquid hydrocarbon per liter of contact space and hour, the improvement which comprises the preliminary steps of admixing with said starting material 65 to 80% by volume of a diluent selected from the group consisting of nitrogen, methane and mixtures thereof, the percentage being calculated upon the total volume of the diluent and the vaporized starting material, and dehydrating the mixture of starting material and diluent to a water vapor content of less than 0.05% by volume.

References Cited in the file of this patent

UNITED STATES PATENTS

2,785,209 Schmetterling ---------- Mar. 12, 1957