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PROCESS FOR THE MANUFACTURE OF PHENYL ESTERS AND PHENOL FROM BENZENE

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ABSTRACT OF THE DISCLOSURE

The invention provides a process for the catalytic preparation of phenyl esters and, if desired, phenol from benzene and saturated aliphatic carboxylic acids in the presence of a catalyst comprising a noble metal of subgroup VIII of the Periodic Table and carboxylates of metals of Group II*b*, III or IV of the Periodic Table.

The present invention relates to an improved process for the manufacture of phenyl esters and, if desired, phenol from benzene.

U.S. patent application Ser. No. 627,679 provides a process for the manufacture of phenyl esters and, if desired, phenol from benzene, which comprises reacting a mixture of benzene, a saturated aliphatic carboxylic acid and molecular oxygen in the presence of at least one noble metal of subgroup VIII of the Periodic Table of Mendeleeff, the stable valency of the metal in its compounds being at most 4.

It has now been found that the activity of the noble metal catalyst in this process and therewith the yields of phenyl ester or phenol can be improved by adding to the noble metal of subgroup VIII of the Periodic Table at least one neutral or basic carboxylate of a metal of Group II*b*, III or IV of the Periodic Table, the atomic number of the latter metal being at most 72.

Suitable metals of Group II*b*, III or IV of the Periodic Table, the neutral or basic carboxylates of which are used in the process of the invention, are, for example, aluminum, titanium and zirconium.

Especially good results are obtained with carboxylates of zinc and cadmium and of the rare earths. The carboxylic acids from which the carboxylates derive are aliphatic or cycloaliphatic carboxylic acids, especially saturated aliphatic or cycloaliphatic carboxylic acids containing up to 10 carbon atoms, for example acetic acid, propionic acid, butyric acid, isobutyric acid and cyclohexane-carboxylic acid. It is advantageous to use the carboxylates of the carboxylic acids used in the reaction with benzene and oxygen or, when the reaction is carried out in the liquid phase, which serve as reaction medium. When acetic acid phenyl ester is to be prepared from acetic acid and benzene it is suitable to use the acetates of the specified metals.

The carboxylates to be used may be neutral, i.e. all valences of the metal atom are bound to carboxylate radicals, for example zinc acetate and aluminum triisobutyrate. It is likewise possible, however, to use basic carboxylates, that is to say compounds in which only some valences of the metal atom are bound to carboxylate radicals while the remaining valences carry oxygen which may be linked via a double bond or by single bonds, for example in the form of one or several hydroxyl groups, such as in zirconyl acetate and aluminum hydroxyacylates.

It is likewise possible, of course, to use mixtures of the specified metal carboxylates.

The concentration of the metal carboxylates may vary within wide limits. An advantageous effect can already be observed with an amount of 5% of the salts, calculated on the content of noble metal in the catalyst. Higher concentrations may also be used, for example up to a multiple of the noble metal content. The carboxylates of the metals of Group II*b*, III or IV of the Periodic Table are preferably used in an amount of from 10 to 100%, calculated on the weight of the noble metal.

Suitable noble metals of subgroup VIII of the Periodic Table are the elements rhodium, iridium, platinum and ruthenium and especially palladium, either alone or in admixture with one another. In addition thereto, the catalyst may contain a small amount, for example up to 50 atom percent, calculated on the noble metal, of metals that are ineffective per se, for example gold, copper, silver, iron and/or manganese.

On principle, the metals of Group II*b*, III, or IV of the Periodic Table may first be used in the form of other compounds, for example in the form of their oxides, hydroxides, carbonates, phosphates or other inorganic salts and the active, neutral or basic carboxylates may be formed in the course of reaction under the action of the carboxylic acid to be reacted, either in the absence or preferably in the presence of a carrier material, for example aluminum oxide, aluminum silicate, silica gel, active carbon, zeolites, pumice, clays or feldspars.

The metal carboxylates to be used according to the invention can be used together with the noble metal of subgroup VIII of the Periodic Table and possibly other activators, for example salts of a strong base and a weak acid; salts forming a buffer system with the carboxylic acid used, for example sodium phosphates or borax; or alkali metal or alkaline earth metal salts of organic acids, preferably alkali metal acetates; and promotors, for example the elements antimony, bismuth, selenium, and tellurium, preferably bismuth and tellurium, in an amount of up to 60 atom percent, preferably 20 to 40 atom percent, calculated on the noble metal, dissolved in a suitable solvent, for example water, for the reaction in the liquid phase or trickle phase. It is advantageous, however, especially when operating in the gaseous phase, to apply the catalyst components either all at once or successively to one of the carrier materials on which they should be distributed as finely as possible. In order to obtain as homogeneous as possible a distribution between the noble metal of subgroup VIII of the Periodic Table and the carboxylates of the metals of Groups II*b*, III and IV of the Periodic Table it is advantageous to prepare the catalyst by reduction of a solution containing reducible compounds of the noble metal. There may be used, for example, aqueous solutions containing simultaneously noble metal chlorides or noble metal nitrates and carboxylates of the metals of Group II*b*, III and IV of the Periodic Table. Alternatively, other soluble salts of the noble metals may be used. As reducing agents in the liquid or gaseous phase inorganic substances, for example sodium boron hydride, hydrazine hydrate or hydrogen; or organic substances, such as ethylene, methanol or ethanol can be used. The preferred proportions by weight of noble metal to carrier metal are in the range of from 0.1 to 10% by weight, or above 10% by weight, advantageously 0.05 to 0.1% by weight. The activator can be used in the liquid phase in an amount from 5 to 30% by weight, preferably 10 to 20% by weight calculated on the benzene/carboxylic acid mixture and in the gaseous phase from 0.1 to 5% by weight, preferably 1 to 3% by weight, calculated on the carrier material.

During the course of the reaction the concentration of the metal carboxylates having an activating action should be maintained as constant as possible in the catalyst. Losses which may occur by a certain volatility of the

compounds during reaction can be readily compensated by adding fresh amounts of the respective metal carboxylates to the reaction components.

The reactants can be mixed within wide limits. As regards the proportion of benzene to oxygen the limits of explosion must be taken into consideration. Temperatures and pressures are not critical either. It is suitable to carry out the reaction at a temperature in the range of from 75 to 300° C., preferably 100 to 250° C. under a pressure of from 1 to 50 atmospheres, preferably 1 to 10 atmospheres. It is likewise possible, however, to operate under subatmospheric or atmospheric pressure. It is advantageous to use benzene and carboxylic acid in equal molar proportions, or an excess of carboxylic acid with respect to benzene. The carboxylic acid should not contain more than 1% of water or it should be used in admixture with its anhydride. When glacial acetic acid is used as starting material it proved advantageous to add up to 30% by weight of acetic anhydride, preferably 10 to 15% by weight, whereby the yield is improved.

The reaction mixture obtained is worked up according to known methods. In the liquid phase process the catalyst is separated from the reaction mixture and again reacted with fresh starting components. When the reaction is carried out in the gaseous or vaporous phase the condensed starting and reaction products are separated, the phenyl ester and phenol, if any, are isolated by distillation and the starting components are reconducted into the reaction.

The reaction product consists of the phenyl ester of the carboxylic acid used or of a mixture of the said phenyl ester with a small amount of phenol. By the concomitant use of the neutral or basic metal carboxylate according to the invention a higher proportion of phenyl ester is formed at the expense of phenol. Moreover, the addition of metal carboxylate considerably increases the activity and efficiency of the catalyst with respect to the formation of phenyl ester.

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

COMPARATIVE EXAMPLE

At a temperature of 180 to 200° C. under a pressure of 4 atmospheres gauge 300 grams of a vaporous mixture of 4 moles of acetic acid and 1 mole of benzene was passed per hour together with 18 liters of oxygen and 9 liters of nitrogen through a reactor containing a catalyst comprising 3% of palladium, 0.3% of gold and 3% of potassium in the form of potassium acetate, supported on 50 milliliters of silicic acid as carrier material. The gas mixture leaving the reactor was cooled and the condensate formed was worked up by distillation. 0.21 gram of acetic acid phenyl ester was obtained per hour, corresponding to a space-time yield of 4.2 grams per liter of catalyst an hour. In addition thereto, a small amount of phenol was obtained.

EXAMPLE 1

The reaction was carried out under the conditions specified in the comparative example with a catalyst comprising 3% of palladium, 0.3% of gold and 3% of cadmium in the form of cadmium acetate, supported on silicic acid. 2.5 grams of acetic acid phenyl ester were obtained per hour, corresponding to a space-time yield of 50 grams per liter of catalyst an hour. Phenol could not be detected.

EXAMPLE 2

The reaction was carried out as defined in Example 1 with the exception that the cadmium acetate replaced by such an amount of zinc acetate that the catalyst contained 3% of zinc. 3.51 grams of acetic acid phenyl ester were obtained per hour corresponding to a space-time yield of 70.1 grams per liter an hour. Phenol could not be detected.

EXAMPLE 3

A silicic acid carrier was impregnated with a solution of palladium acetate, didymium acetate (didymium =commercial mixture of rare earth elements) and potassium acetate in a mixture of acetone and water (proportion about 75:25) and dried at 130° C. The metal acetates were thereby partially reduced. The dried catalyst contained 3% of palladium, 3% of rare earth metals and 0.5% of potassium in bound form.

The reaction was carried out as defined in Example 1 using the catalyst described above. 3.28 grams of acetic acid phenyl ester were obtained per hour, corresponding to a space-time yield of 65.5 grams per liter an hour. Phenol could not be detected.

What is claimed is:

1. In the process for the catalytic preparation of phenyl esters and, if desired, phenol from benzene by reacting a mixture of benzene, a saturated aliphatic or cycloaliphatic carboxylic acid and molecular oxygen in the presence of a metal selected from the group consisting of rhodium, iridium, platinum, ruthenium and palladium, the improvement of adding to the noble metal one neutral or basic carboxylate of the metals selected from the group consisting of zinc, cadmium and a mixture of rare earths known as didymium.

2. The process of claim **1**, wherein an inert carrier is used and alkali metal acetates, used as activators, are present in an amount of from 0.1 to 5% by weight, calculated on the carrier material.

3. The process of claim **1**, wherein the catalyst system contains gold in an amount of up to 50 atom percent, calculated on the noble metal.

4. The process of claim **1**, wherein the reaction is carried out at a temperature in the range of from 100 to 250° C. and under a pressure of from 1 to 10 atmospheres.

5. The process of claim **1**, wherein there are used carboxylates of the carboxylic acids to be reacted with benzene and oxygen to yield the phenyl esters or when operating in the liquid phase which serve as reaction medium.

6. The process of claim **1**, wherein the metal carboxylate is used in an amount of from 10 to 100%, calculated on the weight of the noble metal used.

7. The process of claim **1**, wherein the catalyst system is supported in finely divided form on an inert carrier material.

8. The process of claim **7**, wherein the noble metal is used in a concentration of from 0.1 to 10% by weight, calculated on the carrier material.

9. The process of claim **1**, wherein as carboxylate zinc acetate or cadmium acetate is used.

10. The process of claim **1**, wherein the catalyst system contains as promotor bismuth or tellurium metal in an amount of from 20 to 40 atom percent, calculated on the noble metal.

11. The process of claim **1**, wherein the aliphatic or cycloaliphatic carboxylic acid containing up to 10 carbon atoms to be reacted has a water content of less than 1%.

12. The process of claim **1**, wherein up to 30% by weight of its anhydride are added to the carboxylic acid to be reacted.

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