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(54) Title: METHOD OF MAKING BENZYLATED PHENOLS

(57) Abstract: A method of making benzylated phenols comprises contacting a phenol and a benzyl alcohol with a basic metal oxide catalyst at a temperature sufficient to maintain each of the phenol and the benzyl alcohol in a vapor phase. The phenol has at least one hydrogen ortho to its phenolic hydroxyl group.

WO 2007/027375 A2

METHOD OF MAKING BENZYLATED PHENOLS

BACKGROUND OF THE INVENTION

This disclosure relates to methods of making benzylated phenols.

Benzylated phenols, in particular ortho-benzylated phenols, are valuable as antioxidants and chemical intermediates.

Generally, benzyl phenol is produced by treating phenol with benzyl chloride or benzyl alcohol in the presence of strong acids (e.g., aluminum chloride, zinc chloride, and sulfuric acid). In other methods, 2-benzyl, 2,4-dibenzyl and 2,6-dibenzyl phenols are produced by heating phenol with sodium hydroxide in toluene and reacting it with benzyl chloride. Alternatively benzyl alcohol can be reacted with p-cresol using an aluminum chloride catalyst to make dibenzyl-p-cresol. Vapor phase benzylation of phenols having un-substituted ortho position with benzyl alcohol in contact with an activated alumina catalyst is also known.

However, some of these above described methods produce a substantial amount of meta and para substituted benzyl phenol. Additional problems faced by these methods include batch processing, corrosion, and difficult operating conditions.

Accordingly, a continuing need exists in the art for methods of making benzylated phenols that are selective for making ortho and 2,6-dibenzyl phenols and have less severe operating conditions.

BRIEF DESCRIPTION OF THE INVENTION

Disclosed herein are methods of making benzylated phenols.

According to one embodiment, a method of making benzylated phenols comprises contacting a phenol and a benzyl alcohol with a basic metal oxide catalyst at a temperature sufficient to maintain each of the phenol and the benzyl alcohol in a vapor phase. The phenol has at least one hydrogen located ortho to the phenolic hydroxyl .

DETAILED DESCRIPTION OF THE INVENTION

In this specification and in the claims, which follow, reference will be made to a number of terms which shall be defined to have the following meanings.

The singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

"Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not.

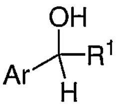
"Combination" as used herein includes mixtures, copolymers, reaction products, blends, composites, and the like.

The endpoints of all ranges reciting the same characteristic are independently combinable and inclusive of the recited endpoint. Values expressed as "greater than about" or "less than about" are inclusive the stated endpoint, e.g., "greater than about 3.5" encompasses the value of 3.5.

Disclosed herein are methods of making benzylated phenols and in particular methods of making ortho phenols (e.g., 2,6-dibenzylphenol). As will be explained in greater detail below, it has been discovered that high selectivity (e.g., 80% to 90%) of ortho benzylated phenols can be obtained by reacting phenols with benzyl alcohols in the presence of a basic metal oxide catalyst at a temperature sufficient to maintain the reactants in a vapor phase. For example, a temperature of 300°C to 600°C can be employed, or, more specifically, a temperature of 350°C to 450°C. Selectivity, as used herein, is defined as 100 X (all ortho benzyl products)/(total products).

The method is applicable to a broad range of phenols. The term "a phenol" is used to generically describe all aromatic hydroxy compounds having at least one hydroxy group bonded to an aromatic ring. The phenol used in the method has at least one hydrogen located ortho to the phenolic hydroxyl group. Further, the phenol is selected such that it is capable of being heated to a temperature sufficient to convert it to the vapor phase without excessive decomposition. Examples of suitable phenols include phenol, o-cresol, p-cresol, 4-ethyl phenol, 4-phenyl phenol, alpha-naphthol, beta-naphthol, 4-chlorophenol, 2-chlorophenol, 2,4-dichlorophenol, 4-bromophenol, hydroquinone, 4-methoxyphenol, 4-ethoxyphenol, and the like, as well as combinations comprising at least one of the foregoing. Particular suitable phenols include the compound phenol, C_6H_5OH, and mono lower alkyl derivatives thereof such as p-cresol, o-cresol, p-ethylphenol, p-n-butylphenol, and the like. More particularly, in one embodiment the phenol is the compound phenol.

The term "benzyl alcohol" broadly describes a class of compounds having the formula I:



(I)

wherein R^1 can be a hydrogen or an alkyl group having 1 to 5 carbons. The Ar represents a monocyclic or polycyclic aromatic group that can be unsubstituted or can be substituted with groups such as alkyl, halogen, alkoxy, and the like. Suitable benzyl alcohols include p-methylbenzyl alcohol, p-ethylbenzyl alcohol, o-methylbenzyl alcohol, p-isobutylbenzyl alcohol, p-chlorobenzyl alcohol, 2,4-dichlorobenzyl alcohol, o-bromobenzyl alcohol, p-methoxybenzyl alcohol, p-ethoxybenzyl alcohol, and the like, as well as combinations comprising at least one of the foregoing. In one embodiment the benzyl alcohol comprises the compound benzyl alcohol, $C_6H_5CH_2OH$.

A wide amount of benzyl alcohol per mole of phenol can be employed in the reaction. For example, the amount of benzyl alcohol per mole of phenol can be 0.2 moles to 10 moles. Within this range, the amount of benzyl alcohol can be greater than or equal to 1 mole of benzyl alcohol per mole of phenol, or, more specifically, greater than or equal to 2 moles of benzyl alcohol per mole of phenol. Also within this range, the amount of benzyl alcohol can be less than or equal to 5 moles of benzyl alcohol per mole of phenol, or, more specifically, less than or equal to 3 moles of benzyl alcohol per mole of phenol.

For example, in one embodiment, when di-benzylation is desired the amount of benzyl alcohol per mole of phenol is 1 mole to 3 moles, or, more specifically, 1.5 moles to 2.5 moles. In other embodiments, high yields (e.g., greater than or equal to 40%) of 2,6-dibenzylphenol are obtained when the amount of benzyl alcohol per mole of phenol is 2 moles to 5 moles, or, more specifically, 3 moles to 4 moles. In another embodiment, when mono-benzylation is desired, the amount of benzyl alcohol per mole of phenol is 0.2 moles of 3 moles, or, more specifically, 0.5 mole to 1 mole.

The catalyst employed in the method includes, as a main constituent, at least one basic metal oxide. Suitable metals for the basic metal oxide, include iron, magnesium, calcium, barium, and strontium. The basic metal oxide can be obtained from a basic metal oxide precursor comprising a magnesium reagent, an iron reagent, or combinations comprising at least one of the foregoing. Any magnesium reagent that yields magnesium oxide can be used. Likewise, any iron reagent that yields iron oxide can be used.

Suitable magnesium reagents include, but are not limited to, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium, basic magnesium carbonate, and mixtures comprising at least one of the foregoing. The magnesium reagent is generally in the form of a powder. For example, the magnesium reagents have an average particle size (as determined by measuring across the major diameter (i.e., the longest diameter) of each particle) of 5 micrometers to 50 micrometers, particularly 10 micrometers to 30 micrometers.

Examples of iron reagents used for the preparation of the catalyst include, but are not limited to, ferric nitrate, ferric sulfate, ferric chloride, ferrous nitrate, ferrous sulfate, and ferrous chloride. In one embodiment the iron reagent comprises ferric nitrate. The iron oxides can be in any form. For example, suitable forms of iron oxides include, but are not limited to, FeO, Fe_2O_3, Fe_3O_4, and mixtures comprising at least one of the foregoing.

The catalyst is formed by dry-blending the basic metal oxide precursor with at least one filler, and an optional pore former. As used in this disclosure, the term "dry blending" refers to the general technique in which the individual ingredients are initially mixed together in the dry state, without resorting to any "wet" techniques, such as suspension blending or precipitation. Any type of mechanical mixer or blender can be used, such as a ribbon blender. The term "filler" is inclusive of, but not limited to, lubricants, binders, and fillers.

The total amount of filler present in the catalyst composition can be less than or equal to 20% by weight, based on the total weight of filler and basic metal oxide precursor. In some embodiments, the total amount of filler is less than or equal to 10% by weight. Examples of fillers used in the catalyst composition include graphite and polyphenylene ether (PPE). In some embodiments the polyphenylene ether is used in an amount of less than or equal to 10% by weight, based on the total weight of the fillers and basic metal oxide precursor. In some embodiments the graphite is employed in an amount less than or equal to 5% by weight.

The optional pore former is a substance capable of aiding the formation of pores in the catalyst. For example, suitable pore formers include, but are not limited to waxes and polysaccharides. The waxes can include paraffin wax, polyethylene wax, microcrystalline wax, montan wax, and the like, as well as combination comprising at least one of the foregoing. The polysaccharide can include cellulose, carboxyl methyl cellulose, cellulose acetate, starch, walnut powder, citric acid, polyethylene glycol, oxalic acid, stearic acid, and the like, as well as combinations comprising at least one of the foregoing. Also useful are anionic and cationic surfactants, generally long chain (C_{10-28}) hydrocarbons containing neutralized acid species (e.g., carboxylic acid, phosphoric acid, and sulfonic acid species).

The optional pore former is employed in an amount sufficient to provide an average pore diameter of 50 angstroms to 300 angstroms after calcination, or, more specifically, 100 angstroms to 300 angstroms after calcination. For example, the pore former can be present in an amount of 0.5 wt.% to 50 wt.%, based on a total weight of basic metal oxide precursor, filler, and pore former. Within this range, the pore former can be present in an amount less than or equal to 40 wt.%, or, more specifically, less than or equal to 30 wt.%. Also within this range, the pore former can be present in amount greater than or equal to 2 wt.%, or, more specifically, greater than or equal to 5 wt.%.

In some embodiments, the catalyst has a bimodal distribution of pores. Without wanting to be bound by theory, it is believed that the first and smaller diameter pore distribution is obtained from the basic metal oxide precursor during the calcination process, i.e. these pores are of similar dimension to those obtained from calcination of the basic metal oxide precursor not containing the pore former. The second and larger diameter pore distribution is believed to be the result of the addition and calcination of the pore former reagent itself, i.e. these pore diameters would not be found in substantial quantities after calcination of a basic metal oxide precursor not containing the pore former.

In one embodiment, the bimodal distribution of pores has a first distribution of pores in which the first distribution has an average pore diameter less than 100 angstroms and a second distribution of pores in which the second distribution has an average diameter greater than or equal to 100 angstroms and less than or equal to 500 angstroms.

After dry-blending of the basic metal oxide precursor, filler (or multiple fillers) and optional pore former is complete, the blended, solid catalyst composition is in the form of a powder. The powder usually has a bulk density of 0.1 grams per cubic centimeter (g/cm^3) to 0.5 g/cm^3, or, more specifically, 0.25 g/cm^3 to 0.5 g/cm^3. The powder then generally undergoes further processing prior to being shaped into a desired form. For example, the power can be sieved (to obtain a more narrow particle distribution), milled, compressed, and the like. In most embodiments, the catalyst composition is deaerated after dry-blending, and prior to additional processing. Deaeration further increases the bulk density of the material by forcibly removing entrained gas (primarily air) from within the powder.

The catalyst can be formed into any desired shape. For example, the catalyst may be compressed into a pellet or "tablet", which can be accomplished by pelletizing equipment, including, but not limited to that equipment described in U.S. Patent

4,900,708. The shaped catalyst composition is then calcined. Calcination is usually carried out by heating the catalyst at a temperature sufficient to convert the basic metal oxide precursor to basic metal oxide, which is the active species in the catalyst. Calcination increases the surface area of the catalyst. The calcination temperature can vary depending on the metal precursor, but is generally 350 °C to 600 °C. The calcination atmosphere can be oxidizing, inert, or reducing. Alternatively, the catalyst can be calcined at the beginning of the benzylation reaction. In other words, calcination can take place in the presence of the feed materials, e.g., phenol and benzyl alcohol.

The surface area of the catalyst pellets can be 50 square meters per gram (m^2/g) to 300 m^2/g, or, more specifically, 120 square meters per gram (m^2/g) to 200 m^2/g, based on BET (Brunauer, Emmett, and Teller) analysis. The uncalcined pellets have pellet density of 1.3 g/cm^3 to 2.1 g/cm^3. Within this range, the pellets have a pellet density of greater than or equal to 1.4 g/cm^3, particularly greater than or equal to 1.6 g/cm^3. Also within this range, the pellets have a pellet density of less than or equal to 2.0 g/cm^3, particularly less than or equal to 1.9 g/cm^3.

In one embodiment, the catalyst pellets have a surface area to volume ratio of 950 square meters per cubic meter (m^2/m^3) to 4000 m^2/m^3. Within this range, the catalyst pellets particularly have a surface area to volume ratio greater than or equal to 1100 m^2/m^3 and more particularly greater than or equal to 1300 m^2/m^3. Also within this range, the catalyst pellets have a surface area to volume ratio less than or equal to 3800 m^2/m^3 and more particularly less than or equal to 3000 m^2/m^3.

In another embodiment, the catalyst pellets have an aspect ratio of 0.7 to 1.0. Within this range, the aspect ratio is particularly greater than or equal to 0.72 and more particularly greater than or equal to 0.75. Also within this range, the aspect ratio is particularly less than or equal to 0.95 and more particularly less than or equal to 0.90. Aspect ratio is herein defined as the ratio of length to diameter or length to width.

In operation, the phenol having at least one position ortho to its phenolic hydroxyl group un-substituted except for hydrogen and the benzyl alcohol are introduced into a vessel containing the catalyst (herein after "catalyst bed" for ease in discussion). The temperature of the catalyst bed is maintained at a temperature sufficient to maintain the reactants in a vapor phase (e.g., a temperature of 300°C to 600°C). The reaction proceeds at atmospheric pressure, but pressures above or below can also be used. This reaction can also be carried out in the presence of water vapor. For example, the water vapor can be present in an amount of 1 wt.% to 35 wt.%, based on a total weight of the reactants, or, more specifically, 5 wt.% to 25 weight%.

The method allows for a selectivity of greater than or equal to 80% of ortho benzylated products (e.g., ortho and 2,6-dibenzyl phenols), or, more specifically, a selectivity of greater than or equal to 85%. In some embodiments, the selectivity is greater than or equal to 99%. Stated another way, embodiments are disclosed where essentially no byproducts are produced. For example, less than or equal to 1 wt.% of the total weight of the reaction products are byproducts (e.g., benzyl ethers, meta or para benzyl phenol). While benzaldehyde may be produced it can be recycled to form ortho benzylated products. When the catalyst includes iron oxide, 15 wt.% orthobenzyl phenol is produced, based on the total weight of the reaction products.

The following examples are provided merely for illustration and representation of an example of making benzylated phenols, and should not be considered as limiting the scope of this disclosure.

EXAMPLES

EXAMPLE 1.

Approximately 10 grams of magnesium carbonate were mixed with 1 gram of wax using a high-speed sheer blender for 10 minutes. The blending process was carried out under liquid nitrogen to allow homogenous mixing. The resulting blend was formed into pellets and calcined at temperatures varying from 390°C to 410°C, using a ramp rate of 0.2 degrees Celsius per minute (°C/min) to 5°C/min under nitrogen. The nitrogen flow was maintained at 0.06 grams of nitrogen per hour per gram (g/hr/g) to 10 g/hr/g of catalyst. The starting temperatures of calcination were also varied from room temperature to 200°C. Approximately 300 milligrams of calcined sample was subjected to surface area and porosity measurement using a Micromeritics 2010 analyzer. The pore size distribution and surface area were obtained from the nitrogen desorption isotherm. The overall average pore diameter was 120 angstroms to 180 angstroms. The pore volume was 0.5 cubic centimeters per gram (cc/g) to 0.7 cc/g. The surface area was 100 m^2/g to 250 m^2/g.

Example 2.

A packed bed reactor was loaded with 5 cubic centimeters (cc) of magnesium carbonate pellets, having an average particle size of 1000 micrometers to 1400 micrometers. This catalyst was calcined in-situ for 16 to 22 hours at 390° C at a rate of 0.2 to 5°C/min under 0.06 to 0.24 (10) g of nitrogen/hr/g of catalyst. All the reactions were performed under atmospheric pressure. After calcination, the temperature was increased from 390°C to 475°C within two hours under nitrogen atmosphere. After 15 minutes of attaining this temperature, a feed mixture was introduced at 0.12 cc/min. The feed contained 16.21 wt.% phenol, 74.48 wt.% benzylalcohol, and 9.31 wt.% water (4:1 molar ratio of benzylalcohol to phenol). The benzylation reaction was carried out under isothermal condition for a period of 24 hours. The yields of reaction products such as ortho benzylphenol, 2,6 dibenzylphenol, benzaldehyde and unconverted phenols and benzylalcohol were monitored over the period of 20 hours. The conversion measured was based on area percent peaks reported by gas chromatography. The results were shown in Table 1.

Table 1

Products	**Yield**
Phenol	1.3
2-benzyl phenol	20.2
2,6-dibenzyl phenol	46.5
Benzaldehyde	13.5
Benzyl alcohol	18.5

This Example illustrates that the yield of ortho-benzylated phenols was greater than 50%, or, more specifically, greater than 60%, when a 4 to 1 molar ratio of benzyl alcohol to phenol was used. More particularly, the yield of 2,6-dibenzyl phenol was greater than or equal to 40%. The reaction demonstrated 83% selectivity for ortho-benzylated phenols with the only other significant product being benzaldehyde which can be recycled to the reaction to produce further product.

In this example, the method uses low cost basic catalyst such as magnesium carbonate, which can be in-situ converted to magnesium oxide. The resultant reaction products include minimal undesired products, such as para and meta benzylphenol. For example reactions employing the catalyst described herein have 13.5% byproduct (only benzaldehyde) compared to 50% byproducts when the same reaction is carried out using alpha alumina.

The method allows for a relatively low cost catalyst to be employed, while allowing for high selectivity to ortho-benzylated phenols. Accordingly, a reduction in separation costs can be realized. Further, this method allows for a continuous method to be employed, which can increase production compared to batch methods. The method does not employ acids that can cause corrosion to or increased cost of process equipment.

While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the invention scope thereof. It is, therefore intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of appended claims.

What is claimed is:

1. A method of making benzylated phenols, the method comprising:

contacting a phenol and a benzyl alcohol with a basic metal oxide catalyst at a temperature sufficient to maintain each of the phenol and the benzyl alcohol in a vapor phase, wherein the phenol has at least one hydrogen located at a position ortho to the phenolic hydroxyl group.

2. The method of Claim 1, wherein the temperature is 300°C to 600°C.

3. The method of Claim 1, wherein the phenol is selected from the group consisting of phenol, o-cresol, p-cresol, 4-ethyl phenol, 4-phenyl phenol, alpha-naphthol, beta-naphthol, 4-chlorophenol, 2-chlorophenol, 2,4-dichlorophenol, 4-bromophenol, hydroquinone, 4-methoxyphenol, 4-ethoxyphenol, and combinations comprising at least one of the foregoing.

4. The method of Claim 1, wherein the benzyl alcohol is selected from the group consisting of benzyl alcohol, p-methylbenzyl alcohol, p-ethylbenzyl alcohol, o-methylbenzyl alcohol, p-isobutylbenzyl alcohol, p-chlorobenzyl alcohol, 2,4-dichlorobenzyl alcohol, o-bromobenzyl alcohol, p-methoxybenzyl alcohol, p-ethoxybenzyl alcohol, and combinations comprising at least one of the foregoing.

5. The method of Claim 1, wherein the basic metal oxide catalyst is obtained from a basic metal oxide precursor comprising a magnesium reagent, an iron reagent, or combinations comprising at least one of the foregoing.

6. The method of Claim 1, wherein the basic metal oxide catalyst comprises a bimodal pore distribution.

7. The method of Claim 6, wherein the bimodal pore distribution comprises a first distribution of pores having an average pore diameter less than 100 angstroms and a second distribution of pores having an average diameter greater than or equal to 100 angstroms and less than or equal to 500 angstroms.

8. The method of Claim 1, wherein the amount of the benzyl alcohol is 0.2 moles to 10 moles of benzyl alcohol per mole of phenol.

9. The method of Claim 8, wherein the amount of benzyl alcohol is 2 moles to 5 moles of benzyl alcohol per mole of phenol.

10. The method of Claim 8, wherein the amount of benzyl alcohol is 0.2 moles to 3 moles of benzyl alcohol per mole of phenol.

11. The method of Claim 1, wherein the basic metal oxide catalyst comprises an average pore diameter of 50 angstroms to 300 angstroms.

12. The method of Claim 1, wherein the basic metal oxide catalyst has a surface area of 50 m^2/g to 300 m^2/g, based on BET analysis.

13. The method of Claim 1, wherein method has a selectivity of greater than or equal to 80% for ortho benzylated products.

14. The method of Claim 13, wherein the selectivity is greater than or equal to 85%.

15. The method of Claim 1, wherein dibenzylated phenol is produced in a yield of greater than or equal to 40%.

16. A method of making benzylated phenols, the method comprising:

contacting a phenol and a benzyl alcohol with a basic metal oxide catalyst at a temperature sufficient to maintain each of the phenol and the benzyl alcohol in a vapor phase;

wherein the phenol has at least one hydrogen located ortho to the phenolic hydroxyl group;

wherein the basic metal oxide catalyst is obtained from a basic metal oxide precursor comprising a magnesium reagent, an iron reagent, or combinations comprising at least one of the foregoing, wherein the catalyst comprises a bimodal pore distribution comprising a first distribution of pores having an average pore diameter less than 100 angstroms and a second distribution of pores having an average diameter greater than or equal to 100 angstroms and less than or equal to 500 angstroms; and

wherein the amount of the benzyl alcohol is 0.2 moles to 10 moles of benzyl alcohol per mole of phenol.

17. The method of Claim 16, wherein the catalyst has a surface area is 50 m^2/g to 300 m^2/g, based on BET analysis.

18. The method of Claim 16, wherein the method has a selectivity greater than or equal to 80% of ortho benzylated products.

19. The method of Claim 18, wherein the selectivity is greater than or equal to 90%.

20. The method of Claim 16, wherein 2,6-dibenzyl phenol is produced in a yield of greater than or equal to 40%.