

## UNITED STATES PATENT OFFICE

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## OXIDATION OF AROMATIC COMPOUNDS

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This invention relates to catalytic vapor phase oxidation of a partially oxidized alkylated benzene and more particularly to the production of polybasic aromatic acids and acid anhydrides.

Hitherto, the practice has been to use specific aromatic hydrocarbons for vapor phase oxidation to certain dicarboxy acids, for example, to use benzene to form maleic anhydride and to use naphthalene or o-xylene to form phthalic anhydride. These dicarboxy acids are formed from the specific aromatic hydrocarbons with difficulty in preventing combustion and undesired side reactions which lower the yields of the desired acids.

An object of this invention is to provide a more selective reaction for producing the desired dicarboxy acids than is obtained in previous practice with the aromatic hydrocarbon feeds.

Another object is to derive further advantages from the use of a partially oxidized alkylated benzene feed, as will become apparent from the following description.

With the present invention, the desired aromatic acids are preferably produced by vapor phase oxidation of an alkyl substituted benzenoid compound having another side chain substituent which contains oxygen linked to carbon adjacent the benzenoid ring.

The partially oxidized compounds to be used as starting material for the vapor phase oxidation may be obtained by alkylation, liquid phase oxidation or other suitable methods. For example, a dialkyl benzene may be partially oxidized in pure form or in mixtures with other hydrocarbons under relatively less vigorous catalyst conditions than those employed in the vapor phase oxidation of the dialkyl benzene to form a dicarboxy acid anhydride.

In general, the oxidized side chain groups in the alkyl benzene compounds to be employed as starting materials for vapor phase oxidation to dicarboxy acids may contain a carbinol, carbonyl, or carboxy function, such as occurs in alkyl-aryl alcohols, aldehydes, ketones, acids, esters, ethers, etc. Alkylated benzenes with more than one side chain partially oxidized, e. g., o-hydroxymethyl benzyl alcohol, may be used also.

For the purpose of illustrating the greater yield efficiency in production of an aromatic dicarboxy acid anhydride from a partially oxidized reactant feed, comparative data are presented in the following examples.

*Example 1*

Ortho-xylene, 1 mol, was oxidized with 100 mols of air at 4,000 v./v./hr. and about 450° C.

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over a  $V_2O_5$  catalyst to phthalic anhydride in 67 mol per cent yield and to maleic anhydride in 7 mol per cent yield.

*Example 2*

Naphthalene under conditions similar to Example 1 was oxidized 76 mol per cent to phthalic anhydride and 8 mol per cent to maleic anhydride.

*Example 3*

Ortho-toluic acid under conditions similar to Examples 1 and 2 was oxidized over 85 mol per cent to phthalic anhydride containing no toluic acid and only traces of maleic anhydride.

In the operation described by Example 3, it is clear that a considerably better yield of phthalic anhydride was obtained by vapor phase oxidation of the partially oxidized starting material than could be obtained directly by vapor phase oxidation of the aromatic hydrocarbon reactants.

The o-toluic acid used as a feed may be obtained by partial oxidation of o-xylene, and such a feed normally contains o-tolualdehyde, o-methyl benzyl alcohol, and other partially oxidized compounds.

Although it is demonstrated that the partially oxidized alkyl aromatic feed material is more selectively oxidized to the aromatic acid anhydride than are the aromatic hydrocarbon feeds under comparable vapor phase conditions with the same proportions of air and with the same conventional type oxidation catalyst, further investigations indicate that the partially oxidized feed material may be more advantageously oxidized in higher concentrations with respect to air or oxygen-containing gas. For example, in oxidizing naphthalene or o-xylene, the concentration of the hydrocarbon reactant in air must be limited to about 1 to 4 mol per cent, whereas, in accordance with the present invention, the concentration of the partially oxidized aromatic compound present in the air feed may be 6 to 10 mol per cent.

With the higher concentration of the organic reactant in the oxygen containing gas, the capacity of the reactor is considerably increased; also, the problem of product recovery is greatly simplified. Furthermore, temperature and heat control is more easily obtained when using the partially oxidized starting material.

Various methods of operation and kinds of apparatus may be used in the vapor phase oxidation of the partially oxidized starting material. The fixed bed, fluid catalyst, or other types of operations applicable in the vapor phase oxida-

tion of the aromatic hydrocarbons may be used, and since such operations are known in the art and are not part of this invention, they will not be described in detail. In the conventional fixed bed operation one of the best catalytic materials to be used is corundum coated with a metal oxide catalyst such as vanadium oxides. In fluid catalyst operations, the catalytic material in finely divided or powdered form is suspended in a moving stream of gaseous reactants, usually passed upwardly through a reaction zone. The suspended particles of catalytic material are put into a turbulent, or fluidized, state within the reaction zone to make effective contact with the reactants. Instead of having the particles carried by the moving stream of gaseous reactants, they may be put in motion countercurrent to the flow of the gaseous reactants. Catalytic materials which are particularly adapted for use with the fluid catalyst technique and in countercurrent motion are hydrous oxide gels, such as silica gel or alumina gel impregnated with a metal oxide catalyst, preferably 10% to 40% by weight of vanadium pentoxide and heat treated at a temperature between 700° C. and 1200° C. These heat-treated, impregnated gels are rugged so that they resist disintegration, have a homogeneous composition, and avoid excessive oxidation or combustion.

With an efficient catalyst, the optimum contact time of the reactants with the catalyst is short, only about 0.05 to 0.9 second, and the optimum contact temperatures are generally within the range of 400° C. to 550° C. With less efficient catalysts, longer contact times, such as 1 to 8 seconds, are used, generally with optimum reaction temperatures within the range of 275° C. to 400° C. The catalyst may comprise one or more oxides of metals in groups V, VI, and VIII of the

periodic system, unsupported or supported by an inert carrier.

It is to be understood that the foregoing examples and described conditions serve as illustrations.

The present invention may be applied more generally and with variations which come within the scope of the appended claims.

We claim:

1. The method of producing a dicarboxy acid, which comprises feeding 0.5 to 10 mol per cent ortho-toluic acid vapor into air to form a reaction mixture, and contacting the mixture with an oxidation catalyst at a temperature in the range of 275° C. to 550° C.

2. The method of producing phthalic anhydride, which comprises reacting vapors of ortho-toluic acid with oxygen at a temperature in the range of 400° C. to 550° C. for less than one second in contact with a fluid catalyst material of silica gel impregnated with vanadium pentoxide and heat treated at a temperature in the range of 700° C. to 1200° C.

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