

PROCESS FOR THE PRODUCTION OF AROMATIC CARBOXYLIC ACIDS IN WATER

This application claims the benefit of U.S. Provisional Application No.

5 60/798,781, filed May 8, 2006.

FIELD OF THE INVENTION

This invention relates generally to the production of aromatic carboxylic acids and, more particularly, to a process for the production of at least one aromatic carboxylic acid in water without the use of bromine.

10 BACKGROUND OF THE INVENTION

Terephthalic acid and other aromatic carboxylic acids are widely used in the manufacture of polyesters, commonly by reaction with ethylene glycol, higher alkylene glycols or combinations thereof, for conversion to fiber, film, containers, bottles and other packaging materials, and molded articles.

15 In commercial practice, aromatic carboxylic acids are commonly made by liquid-phase oxidation in an aqueous acetic acid solvent of methyl-substituted benzene and naphthalene feedstocks, in which the positions of the methyl substituents correspond to the positions of carboxyl groups in the desired aromatic carboxylic acid product, with air or another source of oxygen, which is normally
20 gaseous, in the presence of a bromine-promoted catalyst comprising cobalt and manganese ions. The oxidation is exothermic and yields aromatic carboxylic acid together with byproducts, including partial or intermediate oxidation products of the aromatic feedstock, and acetic acid reaction products, such as methanol, methyl acetate, and methyl bromide. Water is also generated as a byproduct. Aromatic
25 carboxylic acids, typically accompanied by oxidation byproducts of the feedstock, are commonly formed dissolved or as suspended solids in the liquid-phase reaction mixture and are commonly recovered by crystallization and solid-liquid separation techniques.

The exothermic oxidation reaction is commonly conducted in a suitable
30 reaction vessel at elevated temperature and pressure. A liquid-phase reaction

mixture is maintained in the vessel and a vapor phase formed as a result of the exothermic oxidation is evaporated from the liquid phase and removed from the reactor to control reaction temperature. The vapor phase comprises water vapor, vaporized acetic acid reaction solvent and small amounts of byproducts of the oxidation, including both solvent and feedstock byproducts. It usually also contains oxygen gas not consumed in oxidation, minor amounts of unreacted feedstock, carbon oxides and, when the oxygen source for the process is air or another oxygen-containing gaseous mixture, nitrogen and other inert gaseous components of the source gas.

The high temperature and pressure vapor phase generated by liquid-phase oxidation is a potentially valuable source of recoverable acetic acid reaction solvent, unreacted feed material and reaction byproducts, as well as energy. However, its substantial water content, high temperature and pressure and corrosive nature due to components such as gaseous methyl bromide, acetic acid solvent and water pose technical and economic challenges to separating or recovering components for recycle and recovering its energy content. Further, impurities that remain unseparated in recovered process streams can prevent re-use of streams if impurities adversely affect other process aspects or product quality.

Purified forms of aromatic carboxylic acids are usually favored for the manufacture of polyesters for important applications, such as fibers and bottles, because impurities, such as the byproducts generated from the aromatic feedstocks during oxidation and, more generally, various carbonyl-substituted aromatic species, are known to cause or correlate with color formation in polyesters made from the acids and, in turn, off-color in polyester converted products.

Preferred purified forms of terephthalic acid and other aromatic carboxylic acids with lower impurities contents, such as purified terephthalic acid or "PTA", are made by catalytically hydrogenating less pure forms of the acids, such as crude product comprising aromatic carboxylic acid and byproducts generated by the liquid-phase oxidation of the aromatic feedstock or so-called medium purity products, in solution at elevated temperature and pressure using a noble metal catalyst. Purification not only removes impurities from the crude and medium purity products, particularly the major impurity, 4-carboxybenzaldehyde, but also reduces the level of color bodies and the amount of metals, acetic acid and bromine compounds. In

commercial practice, liquid-phase oxidation of alkyl aromatic feed materials to crude aromatic carboxylic acid and purification of the crude product are often conducted in continuous integrated processes in which crude product from liquid-phase oxidation is used as the starting material for purification.

5 A difficulty in the manufacture of aromatic carboxylic acids by such processes results from the use of bromine-promoted oxidation catalysts. Bromine sources used with the catalyst and reaction products thereof formed during oxidation are corrosive. To limit corrosion, process equipment including major equipment items, such as oxidation reactors and off-gas treatment equipment, are normally constructed using
10 titanium or other expensive, corrosion-resistant metals or alloys. Treatment of process off-gases to avoid atmospheric emissions of volatile bromine compounds formed in the process, such as by thermal or catalytic oxidations to oxidize organic bromine compounds to carbon oxides and molecular bromine and reduction of the latter to anionic bromine using sodium formate, are also commonly used, adding
15 complexity and cost to manufacturing processes.

 Eliminating bromine from conventional cobalt-manganese oxidation catalysts is not practical for commercial scale aromatic carboxylic acid manufacture because yields of desired products are unacceptably low. In addition, oxidation of acetic acid solvent for the liquid phase reaction tends to increase substantially in cobalt and
20 manganese-catalyzed oxidations without bromine. Sacrificial promoters, such as methyl ethyl ketone and acetaldehyde, have been proposed as alternatives to bromine, as known from U.S. Patent No. 3,361,803, but their use in practical applications is disfavored because they are consumed in the oxidation process, not only adding costs for replacing the consumed promoter, but also diverting oxygen
25 from the desired reactions of the feedstock. These sacrificial promoters can also negatively affect product quality in higher temperature oxidations. N-hydroxyphthalamide has been reported in Y. Ishii, *J. Mol. Catal. A.: Chem*, 1997, 117 (1-3, *Proceedings of the 6th International Symposium on the Activation of Dioxygen and Homogeneous Catalytic Oxidation*, 1996), 123, as a bromine-free alternative
30 promoter for cobalt - catalyzed reactions, but its utility in manufacture of aromatic carboxylic acids is limited by its low solubility in acetic acid oxidation reaction solvent, and its consumption, and generation of undesirable byproducts during oxidation due to multiple competing decomposition reactions.

German Patent No. 2804158 describes a process for the manufacture of terephthalic acid by a solvent-free co-oxidation of p-xylene and/or p-tolualdehyde plus methyl p-toluate to dimethyl terephthalate using a bromine-free catalyst composed of cobalt or manganese salts or a combination of manganese with cobalt or with zinc salts at a temperature in the range of 140 - 240°C according to the so-called Witten-Hercules process, followed by catalytic hydrogenation of the total reactor effluent from the co-oxidation in the presence of a palladium, platinum, nickel or cobalt catalyst. The process also includes a heat treatment step for transesterification of terephthalate and p-toluate mono- and diesters from either the co-oxidation or hydrogenation step, which is conducted at 180 – 350°C after removal of hydrogen and volatiles. Heat treating is conducted under a nitrogen atmosphere, preferably with addition of water and methanol and, for reducing treatment time, optionally in the presence of Mo, W, Ti, Mg, Ca, Sr, Ba, Mn, Fe, Ni, Zn, Y, K, Y, La, Ce, Nd, Sm, Re, In, Sb, Bi, Se, Te, Sn, P or combinations thereof as catalyst. Absence of bromine from the oxidation catalyst and of monocarboxylic acid reaction solvent in the oxidation are said to permit use of less corrosion-resistant metals for construction of equipment for the co-oxidation and lessen solvent burning.

U.S. Patent No. 6,160,170 (Codignola) discloses oxidation of aromatic feed materials to aromatic carboxylic acids with gaseous oxygen in the absence of bromine in a liquid phase reaction mixture including an aqueous organic solvent using a homogeneous catalytic complex characterized generally as consisting of (A) at least one Group VIIIA metal with a valence greater than 2; and/or at least one Group VIIA metal and/or cerium; and (B) and at least one Group IVA metal which is preferably zirconium or hafnium. (Groups VIIIA, VIIA and IVA referred to in the patent correspond, respectively, to Groups VIII, VIIB and IVB of more recent versions of the Periodic Table according to U.S. Patent Application No. 2002/0188155 A1 (Codignola et al.)) Catalyst compositions described in the patent consist of cerium acetate and zirconium acetate, and of ruthenium oxide and zirconium acetate. Practical effectiveness of the catalysts for the manufacture of aromatic carboxylic acids is limited because water in amounts commonly present in product recovery or other process steps can rapidly convert zirconium (IV) acetate to zirconium (IV) oxide, which, due to its insolubility in water, can be difficult to separate from aromatic carboxylic acid products recovered in solid form, cause plugging of

equipment and catalysts in downstream processing and diminish quality of purified aromatic carboxylic acids products. Precipitated zirconium (IV) oxide also represents a loss of catalyst metal. U.S. Patent Application No. 2002/0188155, noting instability of the catalysts according to International Application WO 98/2938, to which U.S. Patent No. 6,160,170 corresponds, and reduced activity and selectivity due to their degradation, proposes low temperature (90 - 150°C) oxidation using bromine-free catalytic complexes as in the patent preferably containing a Group VIII metal or cerium and zirconium or hafnium and preferably a mixture of cobalt or cerium and zirconium salts, with filtration of the oxidation product and return of mother liquor from filtration to oxidation, all under substantially the same temperature and pressure conditions. In addition to added complexity of the process, catalysts according to this citation show strong activity for oxidation of acetic acid reaction solvent to carbon oxides unless reaction temperatures are maintained below about 120 - 140°C. The oxidation rate in this temperature range is unacceptably low and results in a very long residence time.

International Publication No. WO 2006/068472 discloses a method for the production of terephthalic acid which includes reacting paraxylene, p-toluic acid, 4-carboxybenzaldehyde, or a mixture of two or more thereof, and oxygen in the presence of a heterogeneous catalyst and paraxylene as the solvent. The heterogeneous catalyst described comprises a cobalt and manganese compound, preferably based on a zeolite. The use of paraxylene as a solvent requires that the reaction be run at a decreased rate in order to keep an excessive amount of the terephthalic acid from precipitating, thereby leading to long residence times.

Processes for the production of aromatic carboxylic acids in pure water and in the absence of acetic acid or other organic acid exhibit poor terephthalic acid yield and high feedstock burning. For example, the process disclosed in U.S. Patent No. 3,865,870 for the preparation of aryl carboxylic acids by contacting a mixture of water, methylated benzenes and an oxygen-containing gas with a noble metal catalyst, has a total conversion of less than 40% and high feedstock burning. The process also generates undesirable byproducts resulting from the unwanted dealkylation of the dimethylbenzene, such as paraxylene, to yield benzene and toluene. These dealkylated byproducts must be removed and destroyed.

Pure water processes also require long residence times to achieve modest feedstock conversion at current conventional process conditions. The residence times may be reduced by operating at high oxidation temperatures. For instance, U.S. Patent Application No. 2002/0028968 A1 teaches a process for the production of an aromatic carboxylic acid by contacting in the presence of a catalyst, within a continuous flow reactor, one or more precursors of the aromatic carboxylic acid with an oxidant, wherein the contact is effected with the precursor(s) and the oxidant in a water solvent under supercritical conditions so that one or more precursors, oxidant and water solvent constitute a substantially single homogeneous phase in the reaction zone. The catalyst may comprise one or more heavy metal compounds, such as cobalt and/or manganese compounds, and a bromine promoter. Under these severe conditions, the corrosion due to the presence of bromine is highly aggressive, and the degradation rate of the desired aromatic carboxylic acid is very high. To limit the degradation of the desired product, very careful control of the residence time is crucial.

Accordingly, it would be desirable to provide a process for the production of aromatic carboxylic acids in water without the use of bromine at temperatures and residence times essentially the same as current conventional processes for aromatic carboxylic acid manufacture. Additionally, it would be desirable if such a process produced the aromatic carboxylic acids in high yield with less total burning and with minimal production of undesirable byproducts and carbon oxides

SUMMARY OF THE INVENTION

The process of the disclosure, in its embodiments and features, is directed to the production of at least one aromatic carboxylic acid by contacting a liquid reaction mixture comprising an aromatic feedstock and water with oxygen in the presence of a bromine-free metal catalyst composition wherein the metal catalyst composition has activity in the absence of bromine for oxidation of the aromatic feedstock with at least 80% conversion to oxidized aromatic derivatives of the aromatic feedstock and with at least 80% selectivity to the aromatic carboxylic acid.

According to a first aspect, there is provided a process for the production of at least one aromatic carboxylic acid comprising contacting a liquid reaction mixture comprising an aromatic feedstock and water and no more than a minor amount of C₂₋₈ monocarboxylic acid with oxygen in the presence of a bromine-free metal catalyst composition wherein the metal catalyst composition has activity in the absence of bromine for oxidation of the aromatic feedstock with at least 80% per pass conversion to oxidized aromatic derivatives of the aromatic feedstock and with at least 80% per pass selectivity to the aromatic carboxylic acid.

According to a second aspect, there is provided a process for the production of terephthalic acid comprising contacting a liquid reaction mixture comprising paraxylene and water and no more than a minor amount of C₂₋₈ monocarboxylic acid with oxygen in the presence of a metal catalyst composition free of halogens wherein the metal catalyst composition has activity in the absence of halogens for oxidation of paraxylene with at least 80% per pass conversion to oxidized aromatic derivatives of paraxylene and with at least 80% per pass selectivity to terephthalic acid.

As used herein, "bromine-free" means the absence of reactive bromine in both the metal catalyst composition and the liquid reaction mixture. Unlike conventional commercial catalysts and processes for making aromatic carboxylic

acids such as terephthalic and isophthalic acids, the invented process is "bromine-free" in that it is effective in the substantial or complete absence of bromine sources. While the process, in some of its embodiments, is tolerant of bromine in minor amounts, the presence of bromine in proportions commonly used in conventional commercial processes poisons the catalysts in the inventive process, either deactivating them or shifting selectivity away from aromatic carboxylic acid products toward aromatic species with less fully oxidized substituent groups. Surprisingly, the invention allows for the manufacture of aromatic carboxylic acids, especially terephthalic acid, in high yield and selectivity with minimal production of undesirable byproducts or carbon oxides. In some embodiments, the invention also provides aromatic carboxylic acid yields that surprisingly exceed those achieved with known bromine-free catalyst systems.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for producing at least one aromatic carboxylic acid. In accordance with this invention, a liquid reaction mixture comprising an aromatic feedstock and water is contacted with oxygen in the presence of a bromine-free metal catalyst composition wherein the metal catalyst composition has activity in the absence of bromine for oxidation of the aromatic feedstock with at least 80% conversion to oxidized aromatic derivatives of the aromatic feedstock and with at least 80% selectivity to the aromatic carboxylic acid.

In accordance with one embodiment of this invention, the aromatic feedstocks which may be used include benzene having at least one oxidizable alkyl substituent, naphthalene having at least one oxidizable alkyl substituent, and mixtures thereof. Preferable aromatic feedstocks include paraxylene, metaxylene, pseudocumene, orthoxylene, 2,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene and mixtures thereof. Depending upon which aromatic feedstock is utilized, the current invention may be used to produce terephthalic acid, isophthalic acid, trimellitic acid, phthalic acid, 2,6-naphthalene dicarboxylic acid, 1,5-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid or mixtures thereof. When the current invention is used to produce terephthalic acid (TA), the aromatic feedstock is paraxylene. In addition to the preferable aromatic feedstocks listed above, partially-oxidized derivatives of these feedstocks, such as p-toluic acid, p-tolualdehyde, p-hydroxymethyl benzoic acid, terephthaldehyde, 4-

carboxybenzaldehyde, p-methylbenzyl alcohol and mixtures thereof may also be used in the practice of the present invention.

In accordance with the invention, water is used as the oxidation reaction medium. Although the inventive process does not require the presence of any C₁₋₈ monocarboxylic acids, such as acetic acid, in the reaction medium, minor amounts of such monocarboxylic acids may be present. Oxidation intermediates or other additives, however, may optionally be used to enhance the reactivity of the aromatic feedstock in water. Suitable oxidation intermediates include p-toluic acid, p-tolualdehyde, p-hydroxymethyl benzoic acid, terephthaldehyde, 4-carboxybenzaldehyde, p-methylbenzyl alcohol and mixtures thereof.

In one aspect of this invention, the bromine-free metal catalyst compositions which may be used in the process include homogeneous catalysts, heterogeneous catalysts and mixtures thereof. Preferable homogeneous and heterogeneous catalysts include, but are not limited to, palladium, platinum, vanadium, titanium, tin, antimony, bismuth, molybdenum and mixtures thereof. The homogeneous catalysts which may be utilized are soluble in water to promote contact among catalyst, oxygen and aromatic feedstock. These soluble catalysts may become insoluble, i.e., heterogeneous, during the oxidation reaction. When heterogeneous catalysts are employed, they may be supported or unsupported. If supported, the heterogeneous catalyst comprises an inert support capable of withstanding an acidic process environment without dissolving or significant loss of catalyst metals. Preferred support materials are solids that are stable in the sense of maintaining physical integrity and catalyst metal loadings suitable to process operation over prolonged exposures to process conditions and use. Carbons, high strength, acid stable silicon carbides and various metal oxides such as silicas, aluminas, titanias, including anatase and rutile phases thereof and mixed phase forms, and zirconia are examples of suitable support materials. Preferable supports include carbon, titanium dioxide, silicon dioxide, zirconium dioxide, α -aluminum oxide and mixtures thereof.

In another aspect of this invention, the metal catalyst composition comprises palladium, an element of Group 15 of the Periodic Table of the Elements selected from antimony, bismuth and combinations thereof, and at least one metal or metalloid of Group 4, 5, 6 or 14 of the Periodic Table of the Elements. Groups of the Periodic Table of the Elements referred to herein correspond to "New Notation"

designations according to the Periodic Table of the Elements as found, for example, in the Handbook of Chemistry and Physics, 78th Edition, CRC Press, 1997. The terms "Group" and "Groups" in reference to elements, metals and metalloids will be understood to refer to Groups of such a Periodic Table of the Elements. According to more particular embodiments of the invention, preferred catalyst compositions containing palladium, antimony and one or more of tin, vanadium and molybdenum for use in the inventive process provide surprising conversions of aromatic feedstocks to oxidized aromatic derivatives and selectivities to aromatic carboxylic acids. Proportions of the palladium, antimony, bismuth, Group 4, 5, 6, and 14 metal or metalloid components of the catalyst compositions can vary widely. Preferably, palladium and one or both of antimony and bismuth are present in amounts such that the atom ratio of palladium, to antimony, bismuth or their combination is about 1:1000 to about 1000:1, and more preferably about 1:100 to about 100:1. Proportions of palladium and Group 4, 5, 6 or 14 metal or metalloid also are preferably present in atom ratios of about 1:1000 to about 1000:1 and more preferably about 1:100 to about 100:1. Proportions of metal and metalloid elements in various combinations can be determined and optimized for particular combinations and usages by persons skilled in catalytic oxidations for the manufacture of benzene and naphthalene dicarboxylic acids guided by the description and examples appearing herein.

In yet another aspect of this invention, the metal catalyst composition is also free of halogens other than bromine. The absence of all halogens from the inventive process is preferred since halogens are known to cause undesirable corrosion and adversely affect the activity or selectivity of the metal catalyst compositions. Maximum benefit is achieved by eliminating the use of bromine and not replacing it with one or more other halogens.

Proportions of the aromatic feedstock, catalyst, oxygen and water in oxidation are not critical and vary not only with choice of feed materials and intended product, but also choice of process equipment and operating factors. Oxygen or air or other mixtures of oxygen and nitrogen may be further introduced to contact the aromatic feedstock and metal catalyst composition. The rate of oxygen feed must be at least sufficient to fully oxidize all of the aromatic feedstock to the aromatic carboxylic acid. The concentration of oxygen in any vapor phase of the process should be kept below

about 9% by volume to prevent flammability of any aromatic feedstock and oxygen mixtures. The metal catalyst compositions are suitably used in weights providing about 100 ppm to about 10,000 ppm catalyst metal based on the water plus feed weight.

5 In the practice of the present invention, the liquid reaction mixture comprises from about 0.1% to about 50% aromatic feedstock by weight. Preferably, the liquid reaction mixture comprises from about 5% to about 25% aromatic feedstock by weight.

10 Although the present invention can be carried out as a batch, semi-continuous or continuous process, it is preferred that the process flow move in a continuous mode. Suitable oxidation reactors which may be used in the process include, but are not limited to slurry, CSTR, slurry bubble column, ebulating bed, fixed or packed bed, trickle bed and bubble column reactors. The oxidation reaction may be staged in multiple reactors, if desired, with either feedstock, oxygen or both being introduced in
15 one or more reactors by one or more inlet streams. Depending on the choice of concentrations of reagents and products and other operating parameters, the intermediates and carboxylic acid products may be kept in solution or allowed to solidify in the process after formation. In either case, suitable means to separate products from catalyst and oxidation medium are employed to allow efficient
20 recovery of carboxylic acid product.

The temperature and pressure conditions are preferably selected in order to maintain the oxidation reaction in the liquid phase. The temperature of the liquid reaction mixture during oxidation should be maintained in the range of about 100 °C to about 300 °C and, preferably, in the range of about 170 °C to about 230 °C. Given
25 the physical properties of the system components, these temperatures will result in a system pressure of about 1 bar absolute (bara) to about 100 bara. The liquid reaction mixture is oxidized for about 0.1 hours to about 4 hours and, preferably, for about 0.5 hours to about 2 hours.

30 The process of the present invention effectively produces aromatic carboxylic acids, particularly TA, in high yield without undesirable oxidation byproducts and the need to destroy volatile bromine compounds which result in the generation of more carbon oxides. By contacting a liquid reaction mixture comprising an aromatic

feedstock and water with oxygen in the presence of a bromine-free catalyst composition, the inventors have surprisingly discovered that the aromatic carboxylic acid yields exceed those achieved with known bromine-free catalyst systems. The current process is also economically appealing since savings are achieved through
5 reductions in capital and operating costs. Without the use of reactive bromine or other halogens, the need for expensive corrosion-resistant equipment and the treatment of process off-gases to avoid atmospheric emissions, such as volatile bromine compounds, is eliminated. In addition, the inventive process operates in water in the absence of both monocarboxylic acids and bromine at temperatures and
10 residence times substantially the same as conventional processes for aromatic carboxylic acid manufacture. Furthermore, the current process operates without the burning of any oxidation reaction medium, frequently with less total feedstock burning, and with aromatic carboxylic acid yields and selectivity equivalent to or higher than conventional processes.

EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

Example 1

20 Batch oxidations of p-toluic acid and paraxylene, and semi-continuous oxidations of paraxylene were conducted in water using supported and unsupported catalysts, as shown below in Table 1.

The catalyst compositions used in Example Nos. 1B and 1 D were composed of palladium, antimony and molybdenum loaded at 5 wt%, 5 wt% and 2.5 wt%, and
25 at 5 wt%, 2.5 wt%, and 5 wt%, respectively, on titania and were prepared by calcining in air at 650°C a titania powder obtained from Degussa identified as P25, cooling the titania, and wet impregnating it at room temperature using an aqueous solution containing palladium nitrate, antimony acetate, and ammonium heptamolybdate, which was prepared by mixing individual stock solutions of the salts
30 in relative proportions corresponding to the loading levels of the final composition after calcination. The impregnation technique, also sometimes referred to as excess liquid impregnation, involved the use of a volume of solution that was greater than the total pore volume of the support material. The palladium nitrate stock solution

was an aqueous 35 wt% solution of palladium nitrate. The antimony acetate stock solution was prepared by mixing 5 grams antimony acetate with 10 grams citric acid monohydrate and 30 grams water at 60 °C for 1 hour and then cooling to room temperature. The ammonium heptamolybdate stock solution consisted of 10 grams ammonium heptamolybdate that had been mixed in 20 grams citric acid monohydrate and 60 grams water at 60 °C for 1 hour and which was then cooled to room temperature. After addition of the impregnating solution to the titania, the slurry was homogenized by shaking briefly. The slurry was then dried at 50 °C for 60 hours, heated to 120 °C at a rate of 2 °C per minute, and held at 120 °C for 2 hours. The dried solid was then calcined under flowing air (100 mL/min) by heating slowly (0.4 °C/min) to 400 °C and holding at 400 °C for 2 hours under air flow. The calcined solid was ground to a free-flowing powder and transferred to a crucible. The calcined solid was then reduced with hydrogen by exposure to a flow of dilute hydrogen (7 vol% H₂ in nitrogen) for 1 hour at room temperature and then heating in an oven to 250°C with increases in oven temperature at a rate of 0.4°C/min, after which the temperature was held at 250 °C for 5 hours under dilute hydrogen flow.

The carbon-supported palladium used in combination with antimony and molybdenum acetate salt solutions in Example No. 1C was 5% palladium(0) deposited on activated carbon from the Sigma-Aldrich Chemical Company.

The batch oxidation of p-toluic acid and semi-continuous oxidations of paraxylene were each conducted in water using a fully-supported catalyst (Example No. 1D), a fully-unsupported catalyst (Example No. 1A), and a combination of single-metal supported and other unsupported catalyst components (Example No. 1C) in a 300 mL titanium Parr reactor outfitted with a Magnadrive impeller agitator linked to two liquid feed systems and two parallel water-cooled reflux condensers for receiving overhead gas vented from the reactor. Gas feed to the reactor was controlled by a mass flow controller, the pressure was regulated by a back pressure regulator and vent gases were continuously analyzed for carbon monoxide, carbon dioxide and oxygen by a bank of on-line vent gas analyzers. Heat for the reactor was supplied by a heating mantel, and the heating profile was managed by a Parr controller.

As shown in Table 1, the oxidation runs of Example Nos. 1A, 1C and 1D were begun by charging the reactor bottom with weighed amounts of catalyst or catalyst

components, distilled and deionized water ("D&D Water") as liquid medium for the reaction, and feedstock. In each of Example Nos. 1C and 1D, 2.0 g of p-toluic acid were also added to the reaction mixture. After affixing the reactor bottom to the reactor head, the reactor was filled and pressurized using high pressure bottled nitrogen. The reactor contents were then stirred and heated until a target initiation temperature was reached. Once the reactor contents reached the target initiation temperature, the reactions were begun by replacing the nitrogen flow with a flow of 8 vol% oxygen and 92 vol% nitrogen. For the semi-continuous oxidations, at the time of initiation, a liquid feed of paraxylene was started at a rate of 0.289 mL/min and supplemental water was added at a rate of 0.200 mL/min. The semi-continuous oxidations were conducted for pre-determined periods of time, as reported in Table 1, and then the liquid feed and supplemental water additions were stopped, but the 8% oxygen and 92 % nitrogen flow and constant heating continued for an additional period of time as reported in Table 1.

After the oxidation period ended, the 8% oxygen and 92% nitrogen flow was stopped and nitrogen flow was resumed. The heating mantel was shut off and the reactor and its contents were cooled to room temperature. At that point, the nitrogen flow was shut off, the reactor was depressurized, the reactor bottom was detached and a sample of the total reactor effluent was collected for analysis by high performance liquid chromatography (HPLC). Reaction conditions for Example Nos. 1A, 1C and 1D and results are shown in Table 1.

The batch oxidation of paraxylene in Example No. 1B was conducted by charging a reaction tube, 2 cm in diameter, with the supported catalyst shown in Table 1. The supported catalyst was prepared according to the procedure described above. The reactor was pressurized with air to approximately 45 bar and also to the extent that 10% excess oxygen was present. The reactor was sealed, the reaction mixture was stirred and heated rapidly to a temperature of 220°C. The reaction was run for 90 minutes, and then it was cooled rapidly to room temperature. The reactor was unsealed, and the entire contents of the reactor were dissolved with dimethyl sulfoxide, and the solution was analyzed by HPLC.

As demonstrated in Table 1, the inventive process oxidized a partially-oxidized paraxylene feedstock, as well as unoxidized paraxylene, using catalysts that were fully-unsupported, one-metal supported and unsupported catalyst

- components, and all metals fully-supported. The oxidation of paraxylene occurred in the presence of p-toluic acid (Example Nos. 1C and 1D) and in the absence of such an oxidation intermediate, as in Example No. 1B. The oxidation occurred readily in the presence of water, produced a feedstock conversion of more than 90%, and produced TA having a selectivity of at least 80%. The oxidation off-gas also had a carbon dioxide to carbon monoxide ratio greater than 50:1, indicating minimal production of undesirable byproducts and carbon oxides.

Table 1

Example No.	1A	1B	1C	1D
Feedstock	p-Toluic Acid	Paraxylene		
Oxidation Mode	Batch		Semi-Continuous	
Wt% Loading of Metal(s) on Titania (TiO ₂)	NA	5/5/2.5	5	5/2.5/5
<u>Reactor Charge (g)</u>				
(Pd/Sb/Mo)/TiO ₂	---	0.023	---	4.5051
Pd/Carbon	---	---	5.8514	---
Pd(II) acetate	0.9665	---	---	---
Sb(III) acetate	0.5632	---	0.5230	---
Sn(II) acetate	0.4573	---	---	---
Mo(II) acetate (dimer)	1.2789	---	0.6258	---
D&D water	114.8	0.780	135.2	134.1
Feedstock added	35.73	0.078	22.36	22.36
p-Toluic Acid added	---	0.000	2.0	2.0
Feedstock Conversion (mol%)	91.5	98.2	100	98.3
<u>Oxidation Conditions</u>				
Initiation Temperature (°C)	182	220	210	210
Oxidation Temperature (°C)	196	220	210	210
Main Oxidation Time (min)	90	90	90	90
Tailout Oxidation Time (min)	0	0	15	15
8% Oxygen Flow (SCFH)	15	NA	9	9
Reactor Pressure (psig)	390	*	455	455
<u>Product Selectivity (%)</u>				
Terephthalic Acid	84.06	98.8	90.85	85.37
4-Carboxybenzaldehyde	6.69	0.00	0.60	6.70
p-Toluic Acid	5.70	0.00	0.640	3.88
p-Tolualdehyde	0.07	0.00	0.263	<0.01
Burned Feedstocks	3.49	**	5.20	4.01

<u>Byproducts Selectivity</u>				
Benzoic Acid CO ₂ /CO (mol/mol)	0.007 >50	1.03% **	2.83% >50	0.45% >50

*Reactor pressure was sufficient to maintain the content of the reactor in liquid state.

**Could not obtain this data from the equipment used in Example No. 1B.

Example 2

Example Nos. 2A, 2B and 2C illustrate some of the differences between the
 5 current process in water, a conventional process in water, and a conventional
 process that uses acetic acid as the solvent (See Table 2 below). Both conventional
 processes use cobalt/manganese/bromide catalysts.

Example No. 2A resulted from the oxidation of a mixture in a 70 mL titanium
 reactor. The mixture was prepared by charging a vial with 0.6150 grams of
 10 paraxylene, and then adding 0.5108 g of 6.98 wt% aqueous cobalt(II) dibromide
 solution, 1.5141 grams of 9.83 wt% aqueous manganese(II) dibromide tetrahydrate
 solution, 6.8018 grams of water, and 0.375 grams of Alfonic 810-45 surfactant. The
 heterogeneous mixture was blended at 24,000 rpm and then quickly transferred with
 shaking to the 70 mL reactor. The reactor was sealed and pressurized with air to
 15 500 psig (2.86 grams of air). The sealed reactor was immersed in a sand bath
 heated to 246°C, and shaken at 340 rpm for 15 minutes. The reactor was
 immediately cooled, and a sample of the overhead gas was analyzed for carbon
 monoxide, carbon dioxide and oxygen. A representative sample of the total reactor
 effluent was obtained for analysis by HPLC.

20 Example No. 2B was conducted using the same semi-continuous oxidation
 procedure and equipment as in Example No. 1C above, except that 95% aqueous
 acetic acid was employed as the reaction medium. The reactor was charged with
 0.2206 grams of cobalt(II) acetate tetrahydrate, 0.2320 grams of manganese(II)
 acetate tetrahydrate, 1.546 grams of 48 wt% aqueous hydrobromic acid, and 72.6
 25 grams of 95% aqueous acetic acid. The reactor bottom was attached to reactor
 head and sealed. The reactor contents were flushed and filled with nitrogen to 390
 psig and agitation was initiated. The reactor content was then heated to 182°C. At

that point, the oxidation was initiated when the nitrogen flow was replaced by 8% oxygen and 92% nitrogen flow at 15 standard cubic feet per hour (SCFH), and liquid paraxylene and supplemental 95% aqueous acetic acid addition were initiated at a rate of 0.567 mL/min and 0.633 mL/min, respectively. After 60 minutes had elapsed, the oxidation was discontinued by replacing the 8% oxygen and 92% nitrogen flow with pure nitrogen, and the paraxylene and supplemental 95% aqueous acetic acid additions were terminated. The heating mantel was shutoff and removed, and the reactor was allowed to cool to room temperature. At that time, the reactor was depressurized and unsealed. A sample of the total reactor effluent was obtained for HPLC analysis.

The procedure for Example No. 2C is the same as described above for Example No. 1C.

As demonstrated in Table 2, the conventional process that uses water requires the addition of a surfactant, and very high bromine concentration to activate the catalyst metal ions of cobalt and manganese. The need for a high bromine concentration and the addition of a surfactant are important to obtain a high conversion of paraxylene to produce a high selectivity to TA. This concentration of bromine in water, however, produces a very corrosive environment that requires the use of a highly corrosion-resistant material of construction for the oxidation equipment. Also, it is not desirable to add surfactants to the process since they are contaminants and need to be separated from the final product. Additionally, it is likely that some of the surfactant will be oxidized to undesirable byproducts that need to be removed. The need to remove surfactant byproducts and the need to replenish the surfactant further increase the cost of this process.

The conventional process using acetic acid requires a much lower level of bromine, but to achieve a high conversion of paraxylene and high selectivity to TA, it is necessary to use acetic acid containing a very low concentration of water. This process can tolerate very little water since water causes deactivation. Therefore, in a conventional, acetic acid-based process, energy must be supplied to separate water from the acetic acid in order to maintain a low water concentration in the reaction mixture. The consequence from the use of acetic acid is shown by the solvent burning data in Table 2. The acetic acid "burned" is a significant cost to the conventional process to produce TA. Furthermore, the use of acetic acid and

bromine results in the formation of volatile organic bromides that must be removed by an off-gas oxidation unit. The inventive process, on the other hand, does not require the use of bromine or acetic acid. Instead, in the presence of water, the oxidation of paraxylene occurred in a similar residence time to the conventional acetic acid process, and produced comparable paraxylene conversion and TA. Moreover, there were no volatile byproducts generated like those in a conventional acetic acid and bromine-based process.

Table 2

Example No.	2A	2B	2C
Process	Conventional (Water and Surfactant)	Conventional (Acetic Acid)	Inventive (Water)
Catalyst metals, ppm	4,000	1,000	<6,000
Bromine, ppm	11,533	800	0
Temperature, C	200-250	190-200	190-230
Solvent Burning, kg/te TA	0	19	0
Feedstock Burning, kg/te TA	48	10	45
Residence time, hr	0.25	1.00	1.75
Benzoic acid yield, mole %	4	<1.0	<3
TA Selectivity, %	<92	95	91
CO ₂ /CO ratio in vent gas	9	4	>50

While the present invention is described above in connection with preferred or illustrative embodiments, these embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover all alternatives, modifications and equivalents included within its spirit and scope, as defined by the appended claims.

What is claimed is:

1. A process for the production of at least one aromatic carboxylic acid comprising contacting a liquid reaction mixture comprising an aromatic feedstock and water and no more than a minor amount of C₂₋₈ monocarboxylic acid with oxygen in the presence of a bromine-free metal catalyst composition wherein the metal catalyst composition has activity in the absence of bromine for oxidation of the aromatic feedstock with at least 80% per pass conversion to oxidized aromatic derivatives of the aromatic feedstock and with at least 80% per pass selectivity to the aromatic carboxylic acid.
2. The process of claim 1 wherein the aromatic feedstock is selected from the group consisting of benzene having at least one oxidizable alkyl substituent, naphthalene having at least one oxidizable alkyl substituent, and mixtures thereof.
3. The process of claim 2 wherein the aromatic feedstock is selected from the group consisting of paraxylene, metaxylene, pseudocumene, orthoxylene, 2,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene and mixtures thereof.
4. The process of claim 3 wherein the aromatic feedstock is paraxylene and the aromatic carboxylic acid is terephthalic acid.
5. The process of claim 3 wherein the aromatic feedstock is a partially-oxidized derivative of the aromatic feedstock selected from the group consisting of p-toluic acid, p-tolualdehyde, p-hydroxymethyl benzoic acid, terephthaldehyde, 4-carboxybenzaldehyde, p-methylbenzyl alcohol and mixtures thereof.
6. The process of claim 1 wherein the metal catalyst composition is selected from the group consisting of a homogeneous catalyst, a heterogeneous catalyst and mixtures thereof.
7. The process of claim 6 wherein the metal catalyst composition is selected from the group consisting of palladium, platinum, vanadium, titanium, tin, antimony, bismuth, molybdenum and mixtures thereof.

8. The process of claim 6 wherein the heterogeneous catalyst is on an inert support.
9. The process of claim 8 wherein the inert support is selected from the group consisting of carbon, titanium dioxide, silicon dioxide, zirconium dioxide, α -aluminum oxide and mixtures thereof.
10. The process of claim 1 wherein the metal catalyst composition is free of halogens other than bromine.
11. The process of claim 1 wherein an oxidation intermediate selected from the group consisting of p-toluic acid, p-tolualdehyde, p-hydroxymethyl benzoic acid, terephthaldehyde, 4-carboxybenzaldehyde, p-methylbenzyl alcohol and mixtures thereof is added to the liquid reaction mixture.
12. The process of claim 1 wherein the liquid reaction mixture comprises from about 0.1% to about 50% aromatic feedstock by weight.
13. The process of claim 1 wherein the liquid reaction mixture comprises from about 5% to about 25% aromatic feedstock by weight.
14. The process of claim 1 wherein the liquid reaction mixture is contacted at a temperature in the range of about 100 °C to about 300 °C.
15. The process of claim 1 wherein the liquid reaction mixture is contacted at a temperature in the range of about 170 °C to about 230 °C.
16. The process of claim 1 wherein the liquid reaction mixture is contacted for about 0.1 hours to about 4 hours.
17. The process of claim 1 wherein the liquid reaction mixture is contacted for about 0.5 hours to about 2 hours.
18. A process for the production of terephthalic acid comprising contacting a liquid reaction mixture comprising paraxylene and water and no more than a minor amount of C₂₋₈ monocarboxylic acid with oxygen in the presence of a metal catalyst composition free of halogens wherein the metal catalyst composition has activity in the absence of halogens for oxidation of paraxylene with at least 80% per pass conversion to oxidized aromatic derivatives of paraxylene and with at least 80% per pass selectivity to terephthalic acid.

19. The process of claim 18 wherein the metal catalyst composition is selected from the group consisting of palladium, platinum, vanadium, titanium, tin, antimony, bismuth, molybdenum and mixtures thereof.
- 5 20. The process of claim 18 wherein an oxidation intermediate selected from the group consisting of p-toluic acid, p-tolualdehyde, p-hydroxymethyl benzoic acid, terephthaldehyde, 4-carboxybenzaldehyde, p-methylbenzyl alcohol and mixtures thereof is added to the liquid reaction mixture.
21. The process of claim 1 wherein the reaction mixture is free of C₂₋₈ monocarboxylic acid.
- 10 22. The process of claim 18 wherein the reaction mixture is free of C₂₋₈ monocarboxylic acid.