which metal precursor deposition takes place can range from at or below ambient up to about 120°C depending upon the deposition process selected, and those of ordinary skill in the art may readily select the appropriate deposition process and conditions to effectuate the deposition of the metal-containing compounds onto (and into) the support.

[0027] After the addition of the metal-containing compounds to the support, the metal-containing catalyst precursor may be dried. Drying may be conducted at ambient temperature or at an elevated temperature up to about 120°C. Preferably, drying is conducted at a temperature in the range of about 40°C to about 90°C and more preferably at a temperature at least about 60°C. The drying step may be conducted for a period of time ranging from about a few minutes to a few days. Typically, the drying time is in the range of about 6 hours to about 24 hours. Drying of the catalyst precursor can be conducted, for example, on a band dryer, in a direct fired rotary oven, or in an indirect fired rotary oven. When using physical coating for the metal deposition, drying may be done simultaneously with the coating step in the coating chamber. After deposition of the metal precursors an auxiliary chemical agent (e.g. precipitation agent) may be added, either before and/or after drying, to convert the precursors into more easily reducible or thermally decomposable forms.

[0028] After drying, the support having the precursor compound deposited thereon and, possibly, therein is typically subjected to at least one thermal treatment, under oxidative (calcination), inert (nitrogen, argon) and/or reductive (gas phase or liquid phase reductants) conditions, as is necessary for the metals of the catalyst, in order to convert the platinum and rhodium deposited thereon to Pt(0) and Rh(0). In some embodiments, the catalysts may be calcined and then the metal may be further reduced to Pt(0) and Rh(0) in-situ (i.e., in the reactor). In the case of platinum, the platinum of the compound is reducible to Pt(0) upon thermal treatment regardless of whether the atmosphere is oxidizing, inert or reducing. Thus, thermal treatment(s) may, for example, be conducted in air. Preferably, the substantial decomposition of the Pt precursor occurs during calcination and at least a portion of the platinum is converted to Pt(0). In the case of rhodium, the rhodium is preferably reduced to Rh(0) under reducing atmosphere conditions. Therefore, in various embodiments, the thermal treatment(s) is (are) conducted under a hydrogen gas containing atmosphere; alternatively, a liquid reducing agent may be employed to reduce the metals to platinum(0) and rhodium(0) on the support: for example, hydrazine, formaldehyde, formic acid, sodium formate or sodium hypophosphite may be employed to effect the requisite reduction.

[0029] The temperature(s) at which the calcination treatment(s) is (are) conducted generally range from about 150°C to about 600°C. More typically, the temperature(s) of the thermal treatment(s) range from about 200°C to about 550°C. The thermal treatment is typically conducted for a period of time ranging from about 1 hour to about 16 hours. More typically, the treatment is conducted for a period of time ranging from about 2 hours to about 12 hours. For example, at a thermal treatment temperature of about 350°C, the time of the treatment at temperature is in the range of about 2 hours to about 6 hours.

[0030] When a thermal treatment is conducted under a hydrogen gas-containing atmosphere – a reducing atmosphere – the thermal treatment under such gas phase reductive conditions is generally conducted at a temperature range from about 100°C to about 500°C. When the thermal treatment is conducted in the presence of a liquid phase reducing agent, the thermal treatment under liquid phase reductive conditions is conducted at a temperature range from about 20°C to about 95°C. It should be understood that a thermal treatment under reductive conditions can optionally be conducted in situ in a chemical reactor prior to the use of the catalyst given the reaction temperatures typically employed, for example, in the production of an adipic acid product from glucaric acid substrate. In various embodiments, a thermal treatment under reducing conditions can be conducted subsequent to a calcination treatment.

[0031] Optionally, a washing step can be employed after a thermal treatment to remove non-decomposable counterion(s) of the metal precursor compounds, such as Na, K, Cl. Typical wash solutions can include, for example, water, alcohols, polyols, carboxylic acids, or mixtures thereof. The wash solution may optionally contain a chemical reagent that will complex the counterion(s).

[0032] The reduced metals deposited on the outer surfaces of the support are in the form of metallic particles: that is to say, the platinum on the fresh catalyst exists substantially as particles of substantially platinum (0) and the rhodium on the fresh catalyst exists substantially as particles of rhodium (0). We have discovered that, although the particles sizes vary, the metallic particles of the catalysts of the present invention are substantially of a size in the range of at least about 1 nanometer (nm) and less than or equal to about 30 nanometers (nm). By "size" we mean the largest, straight line dimension of the particle. By "substantially" we mean at least about 50%. More typically, the particles are substantially of a size equal to or less than about 20 nm and, preferably, in the range of about 2 nm to about 20 nm (See, for example, the fresh catalyst

[0045] In preferred embodiments, the adipic acid product of formula II comprises adipic acid.

[0046] In the above reaction, a hydrodeoxygenation substrate is converted to an adipic acid product by catalytic hydrodeoxygenation in which carbon-hydroxyl groups are converted to carbon-hydrogen groups. In various embodiments, the catalytic hydrodeoxygenation is hydroxyl-selective wherein the reaction is completed without substantial conversion of the one or more other non-hydroxyl functional group of the substrate.

[0047] The halogen source may be in a form selected from the group consisting of atomic, ionic, molecular, and mixtures thereof. Halogen sources include hydrohalic acids (e.g., HCl, HBr, HI and mixtures thereof; preferably HBr and/or HI), halide salts, (substituted or unsubstituted) alkyl halides, or elemental halogens (e.g. chlorine, bromine, iodine or mixtures thereof; preferably bromine and/or iodine). In various embodiments the halogen source is in molecular form and, more preferably, is bromine. In more preferred embodiments, the halogen source is a hydrohalic acid, in particular hydrogen bromide.

[0048] Generally, the molar ratio of halogen to the hydrodeoxygenation substrate is about equal to or less than about 1. In various embodiments, the mole ratio of halogen to the hydrodeoxygenation substrate is typically from about 1:1 to about 0.1:1, more typically from about 0.7:1 to about 0.3:1, and still more typically about 0.5:1.

[0049] Generally, the reaction allows for recovery of the halogen source and catalytic quantities (where molar ratio of halogen to the hydrodeoxygenation substrate is less than about 1) of halogen can be used, recovered and recycled for continued use as a halogen source.

[0050] Generally, the temperature of the hydrodeoxygenation reaction mixture is at least about 200°C, typically at least about 800°C, and more typically at least about 1000°C. In various embodiments, the temperature of the hydrodeoxygenation reaction is conducted in the range of from about 200°C to about 2500°C, from about 800°C to about 2000°C, more preferably from about 1200°C to about 1800°C, and still more preferably between about 1400°C and 1800°C. Typically, the partial pressure of hydrogen is at least about 25 psia (172 kPa), more typically at least about 200 psia (1379 kPa) or at least about 400 psia (2758 kPa). In various embodiments, the partial pressure of hydrogen is from about 25 psia (172 kPa) to about 2500 psia (17237 kPa), from about

EXAMPLES

[0057] The following non-limiting examples are provided to further illustrate the present invention.

General description of the synthesis of the exemplified Pt/Rh catalysts (by incipient wetness impregnation)

[0058] An aqueous solution of a platinum precursor compound and rhodium precursor compound was added to supports of zirconia, titania, silica, carbon, zeolite and montmorillonite in the form of particles (Examples 1-4) and extrudate (Example 5) in multiple portions. The metal precursor solution was either pipetted or sprayed onto the support for the impregnation. Each mixture was agitated to evenly impregnate the support. Each sample was dried in a 60θ°C oven or at room temperature overnight under a dry air purge. Each sample was then reduced under forming gas (5% H_2 and 95% N_2) atmosphere typically at 350θ°C for 6 hours with 2θ°C/min temperature ramp rate. By adjusting the concentrations of the solutions of the platinum and rhodium precursor compounds, a series of catalysts with various metal loadings and molar ratios of Rh and Pt were prepared.

[0059] As illustrated in the examples to follow, different metal precursor compounds can be used to prepare catalysts with various Rh and Pt metal loadings and molar ratios of Rh and Pt on different supports. When the Rh and Pt precursor compounds were found to be incompatible (meaning formation of precipitate upon contact of solutions), one metal precursor solution was added to the support to impregnate the support with one metal, followed by drying in a 60θ°C oven or at room temperature overnight under a dry air purge, and subsequent addition of the other metal precursor solution was undertaken to impregnate the single metal containing support with the other metal. The material was further dried in a 60θ°C oven or at room temperature overnight under a dry air purge.

Example 1: Synthesis of Pt/Rh zirconia catalyst by incipient wetness impregnation (single fix)

[0060] An aqueous solution of platinum nitrate and rhodium nitrate (20 ml in total volume containing 0.41 g Rh and 1.17 g Pt) was added to a zirconia support (100 g, 90-180 1m particle size) in multiple portions using a pipette over a period of 10 min. During the addition of the solution, the mixture was agitated to evenly impregnate the support. The sample was dried in a

60θ°C oven overnight under a dry air purge. The sample was then reduced under forming gas (5% H_2 and 95% N_2) atmosphere at 350θ°C for 6 hours with 2θ°C/min temperature ramp rate. The final catalyst contained 0.41 wt% Rh and 1.17 wt% Pt.

Example 2: Synthesis of Pt/Rh zirconia catalyst by incipient wetness impregnation (separate fix)

[0061] An aqueous solution of $(NH_3)_6Rh(OH)_3$ (10 ml in total volume containing 0.12 g Rh) was added to a zirconia support (50 g, 90-180 1m particle size) in multiple portions using a pipette over a period of 5 min. During addition of the solution, the mixture was agitated to evenly impregnate the support. The sample was dried in a 60θ°C oven overnight under a dry air purge and then cooled to room temperature. To this material, an aqueous solution of platinum nitrate (10 ml in total volume containing 0.27 g Pt) was added in multiple portions using a pipette over a period of 5 min. During addition of the solution, the mixture was agitated to evenly impregnate the support. The sample was dried in a 60θ°C oven overnight under a dry air purge. The sample was then reduced under forming gas (5% H_2 and 95% N_2) atmosphere at 350θ°C for 6 hours with 2θ°C/min temperature ramp rate. The final catalyst contained 0.24 wt% Rh and 0.54 wt% Pt.

Example 3: Use of Pt/Rh catalysts for selective hydrodeoxygenation of glucaric acid monolactone in a batch reactor

[0062] Catalyst (20 mg) produced in accordance with the general description set forth hereinabove was weighed into a glass vial insert, followed by addition of a solution (100 11 in total volume) containing glucaric acid monolactone (0.8 M) and HBr (0.6 M) in acetic acid. The glass vial insert was loaded into a pressure reactor and the reactor was closed. The atmosphere in reactor was replaced with hydrogen and pressurized to 900 psig at room temperature. Reactor was heated to 160θ°C and maintained at 160θ°C for 1.5 hours with orbital shaking. After 1.5 hours, the shaking was stopped and reactor was cooled to 40θ°C. Pressure in reactor was then slowly released. The glass vial insert was removed from reactor and centrifuged. The clear solution was diluted with deionized water and analyzed by Fast-MS (with deuterated adipic acid d-8 as internal standard) and HPLC to determine the yield of adipic acid. A selection of results is shown in Table 1. Weight percentages of metals are nominal weight % on a total catalyst weight basis.

effective for the selective hydrodeoxygenation of glucaric acid monolactone without any appreciable loss of catalyst activity during the 100 hour test. The Pt/Rh titania catalyst showed an appreciable loss of activity during the 100 hour test.

Example 5: Synthesis and testing of a Pt/Rh zirconia extrudate catalyst in a flow reactor

[0064] An aqueous solution of platinum nitrate and rhodium nitrate (20 ml in total volume containing 0.20 g Rh and 0.60 g Pt) was sprayed onto a zirconia support (100 g, 1.5×1.5 mm extrudate) over a period of 20 min. During addition of solution, the mixture was agitated to evenly impregnate the support. The sample was dried at room temperature overnight under a dry air purge in a 500 ml round bottom flask on a rotary evaporator with gentle tumbling. The sample was then reduced under forming gas (5% H_2 and 95% N_2) atmosphere at 350°C for 6 hours with 2°C/min temperature ramp rate. The final catalyst contained 0.20 wt% Rh and 0.60 wt% Pt located in a shell on the surface of the extrudate. This catalyst was effective for the selective hydrodeoxygenation of glucaric acid monolactone in a continuous flow fixed bed reactor over a period of 1000 hours without any appreciable loss of catalyst activity.