practice of this invention it is possible to attain a Relative Activity of at least 80 and up to about 2000.

Other aspects and advantages of the present invention are described in the detailed description below and in the claims.

Brief Description of the Drawings:

The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts. In the **Figures:**

Figure 1 is a schematic diagram of an apparatus suitable for producing vinyl ester from a carboxylic acid and acetylene in accordance with the process of the present invention;

Figure 2 is a process flow diagram illustrating one suitable industrial scale system for the production of vinyl ester from a carboxylic acid and acetylene according to this invention;

Figure 3 is an illustration of the relative selectivity to vinyl benzoate achieved using a variety of catalyst metals according to the process of the invention; and

Figure 4 is an illustration of the Relative Activity achieved using a variety of catalyst metals according to the process of the invention.

Detailed Description of the Invention

The invention is described in detail below with reference to several embodiments and numerous examples. Such discussion is for purposes of illustration only. Modifications to particular examples within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent

to one of skill in the art. Terminology used herein is given its ordinary meaning consistent with the exemplary definitions set forth immediately below.

As used herein, a heterogeneous catalyst refers to a catalyst that is in a different phase than the reactants during catalysis. In order for the reaction to occur, one or more of the reactants must diffuse to the catalyst surface and adsorb onto it. After reaction, the products must desorb and diffuse away from the surface. In contrast, as used herein a homogeneous catalyst refers to a catalyst that is present in the same phase as the reactants.

Mole percent (mole %) and like terms refer to mole percent unless otherwise indicated. Weight percent (wt % or %) and like terms refer to weight percent unless otherwise indicated.

"Conversion" refers to the fraction of reactant consumed in the reaction and is expressed as a mass percentage based on the amount of carboxylic acid in the feed. The conversion of carboxylic acid (CA) is calculated from gas chromatography (GC) data using the following equation:

$$\text{CA conversion (\%)} = 100 * \frac{\text{mass CA, in} - \text{mass CA, out (GC)}}{\text{mass CA, in}}$$

where mass CA, in = mass of carboxylic acid loaded (weighed in) into the reactor, and mass CA, out (GC) = mass of carboxylic acid after the reaction based on GC data.

"Selectivity" refers to the amount of vinyl ester produced relative to the carboxylic acid consumed and is expressed as a mole percent based on converted carboxylic acid. For example, if the conversion is 50 mole % and 50 mole % of the converted carboxylic acid is converted to vinyl ester, we refer to the vinyl

REPLACEMENT PAGE

Brief Description of the Drawings:

The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts. In the **Figures:**

Figure 1 is a schematic diagram of an apparatus suitable for producing vinyl ester from a carboxylic acid and acetylene in accordance with the process of the present invention;

Figure 2 is a process flow diagram illustrating one suitable industrial scale system for the production of vinyl ester from a carboxylic acid and acetylene according to this invention;

Figure 3 is an illustration of the relative selectivity to vinyl benzoate achieved using a variety of catalyst metals according to the process of the invention; and

Figure 4 is an illustration of the Relative Activity achieved using a variety of catalyst metals according to the process of the invention.

Detailed Description of the Invention

The invention is described in detail below with reference to several embodiments and numerous examples. Terminology used herein is given its ordinary meaning consistent with the exemplary definitions set forth immediately below.

As used herein, a heterogeneous catalyst refers to a catalyst that is in a different phase than the reactants during catalysis. In order for the reaction to occur, one or more of the reactants must diffuse to the catalyst surface and adsorb

showed that TONs were below 0.1 for most of the catalysts in this group, and none of the TONs exceeded 20.

While the invention has been described in connection with several embodiments, modifications of those embodiments within the spirit and scope of the present invention will be readily apparent to those of skill in the art. The invention is defined in the appended claims.

WHAT IS CLAIMED IS:

1. A heterogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid optionally dissolved in a suitable organic solvent with acetylene in the presence of a supported metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives or a mixture thereof; wherein said supported metal is selected from the group consisting of iridium, palladium, platinum, rhenium, rhodium and ruthenium; and wherein the catalyst and optionally the ligand(s) and additive(s) are selected and utilized in amounts such that selectivity to the vinyl ester is at least 50%.

2. The process according to Claim 1, wherein the process is further characterized by a carboxylic acid conversion of at least 50% and a relative activity of at least 80.

3. The process according to Claim 1, wherein said carboxylic acid is selected from the group consisting of benzoic acid, 2-ethyl hexanoic acid, neopentanoic acid, neoheptanoic acid and neodecanoic acid.

4. The process according to Claim 1, wherein the catalyst support is selected from the group consisting of carbon, activated carbon, graphite, silica, titania, alumina, calcium silicate, calcium carbonate, silica-alumina, silica aluminate, zirconia, barium carbonate and barium sulfate.

5. The process according to Claim 1, wherein the supported metal catalyst is present on the catalyst support at a loading level of about 0.1 weight percent to about 20 weight percent.

6. The process according to Claim 1, wherein an initial reaction mixture comprises a mixture of said supported metal catalyst and carboxylic acid in a molar acid:metal ratio of from about 4000:1 to about 300:1.

7. The process according to Claim 1, wherein the reaction temperature ranges from about 25°C to about 250°C.

8. The process according to Claim 1, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.

9. The process according to Claim 1, wherein the solvent is selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

10. The process according to Claim 1, wherein said ligand is selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, diphenyl-2-pyridylphosphine, oxydi-2,1-phenylenebis(diphenyl-phosphine), tris(p-trifluoromethylphenyl)phosphine [$P(p\text{-}CF_3C_6H_4)_3$], tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine and tris(4-methoxyphenyl)phosphine; and said additive is selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tert-butylammonium acetate.

11. A heterogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid, optionally dissolved in

a suitable organic solvent, with acetylene in the presence of a supported platinum metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives thereof; wherein the catalyst and optionally the ligand(s) and additive(s) are selected and utilized in amounts such that the relative activity is at least 100.

12. The process according to Claim 11, wherein said carboxylic acid is benzoic acid.

13. The process according to Claim 11, wherein said carboxylic acid is 2-ethylhexanoic acid.

14. The process according to Claim 11, wherein the catalyst support is carbon, activated carbon, alumina or titania.

15. The process according to Claim 11, wherein the loading level of the metal is from about 0.1 weight percent to about 10 weight percent.

16. The process according to Claim 11, wherein the carboxylic acid and catalyst are provided in a molar acid:metal ratio of from about 3000:1 to about 380:1.

17. The process according to Claim 11, wherein the reaction temperature ranges from about 50°C to about 180°C.

18. A heterogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a supported platinum catalyst and optionally in the presence of triphenylphosphine as a ligand, and optionally an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine, wherein the platinum loading of the catalyst is from

about 0.5 weight % up to about 10 weight %, the support is selected from carbon, activated carbon, titania, alumina, or zirconia, and the benzoic acid is provided in a molar ratio of benzoic acid:platinum metal of about 300:1 to about 4000:1.

19. The process according to Claim 18, wherein the catalyst support is carbon, activated carbon, or titania.

20. The process according to Claim 18, wherein the reaction temperature ranges from about 100°C to about 180°C.

21. A heterogeneous process for the selective formation of vinyl 2-ethylhexanoate from 2-ethylhexanoic acid which comprises reacting 2-ethylhexanoic acid with acetylene, optionally in a suitable organic solvent, at a suitable temperature and pressure in the presence of a supported platinum catalyst, optionally in the presence of triphenylphosphine as a ligand, and optionally in the presence of an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine, wherein the platinum loading of the catalyst is from about 0.5 weight % up to about 10 weight %, the support is selected from carbon, activated carbon, titania, alumina, or zirconia, and the 2-ethylhexanoic acid is provided in a molar ratio of 2-ethylhexanoic acid:platinum metal of about 300:1 to about 4000:1.

22. The process according to Claim 21, wherein the reaction temperature ranges from about 140°C to about 200°C.

23. The process according to Claim 21, wherein the support is carbon or activated carbon and wherein the platinum is present at a loading level of from about 0.5 weight percent to about 6 weight percent.

24. The process according to Claim 21, wherein the support is carbon and the ligand is triphenylphosphine.

25. The process according to Claim 21, wherein the supported platinum catalyst is 0.5 weight percent platinum supported on carbon.

26. The process according to Claim 21, wherein the supported platinum catalyst is one (1) weight percent platinum supported on carbon.

27. The process according to Claim 21, wherein the supported platinum catalyst is three (3) weight percent platinum supported on carbon.

28. The process according to Claim 21, wherein the supported platinum catalyst is a combination of palladium and platinum and the support is carbon, and wherein the palladium and platinum are present at a loading level of from about 1 weight percent to about 5 weight percent.

29. The process according to Claim 21, wherein the supported platinum catalyst is one (1) weight percent platinum on carbon and the reaction temperature is about 160°C.

30. A heterogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a temperature in the range of about 100°C to about 180°C in the presence of a supported platinum catalyst chosen from 1% platinum on carbon, 3% platinum on activated carbon, 5% platinum on titania or 0.5% platinum on alumina and optionally in the presence of triphenylphosphine as a ligand, and optionally an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine.

31. The process according to Claim 30, wherein the reaction temperature ranges from about 110°C to about 170°C.

32. The process according to Claim 30, wherein the reaction temperature ranges from about 120°C to about 160°C.

33. The process according to Claim 30, wherein the supported metal catalyst is five (5) weight percent platinum supported on titania.

34. The process according to Claim 30, wherein the selectivity to vinyl ester based on carboxylic acid consumed is at least 60 percent.

WHAT IS CLAIMED IS:

1. A heterogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid optionally dissolved in a suitable organic solvent with acetylene in the presence of a supported metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, diphenyl-2-pyridylphosphine, oxydi-2,1-phenylenebis(diphenyl-phosphine), tris(p-trifluoromethylphenyl)phosphine [$P(p\text{-}CF_3C_6H_4)_3$], tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine and tris(4-methoxyphenyl)phosphine, or optionally in the presence of one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tert-butylammonium acetate, or a mixture thereof; wherein said supported metal is selected from the group consisting of palladium, platinum, and rhodium; and wherein reaction temperature and pressure, the catalyst and optionally the ligand(s) and additive(s) are selected such that selectivity to the vinyl ester is at least 50%; and wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic, neoheptanoic, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

2. The process according to Claim 1, wherein the process is further characterized by a carboxylic acid conversion of at least 50% and a relative activity of at least 80.

3. The process according to Claim 1, wherein said carboxylic acid is selected from the group consisting of benzoic acid, 2-ethyl hexanoic acid, neopentanoic acid, neoheptanoic acid and neodecanoic acid.

4. The process according to Claim 1, wherein the catalyst support is selected from the group consisting of carbon, activated carbon, graphite, silica, titania, alumina, calcium silicate, calcium carbonate, silica-alumina, silica aluminate, zirconia, barium carbonate and barium sulfate.

5. The process according to Claim 1, wherein the supported metal catalyst is present on the catalyst support at a loading level of about 0.1 weight percent to about 20 weight percent.

6. The process according to Claim 1, wherein an initial reaction mixture comprises a mixture of said supported metal catalyst and carboxylic acid in a molar acid:metal ratio of from about 4000:1 to about 300:1.

7. The process according to Claim 1, wherein the reaction temperature ranges from about 25°C to about 250°C.

8. The process according to Claim 1, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.

9. The process according to Claim 1, wherein the solvent is selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

10. The process according to Claim 1, wherein the catalyst includes a ligand selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, diphenyl-2-pyridylphosphine, oxydi-2,1-phenylenebis(diphenyl-phosphine), tris(p-trifluoromethylphenyl)phosphine [$P(p\text{-}CF_3C_6H_4)_3$], tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine and tris(4-methoxyphenyl)phosphine; and optionally one or more additives, ~~is~~ selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tert-butylammonium acetate, are present.

11. A heterogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid, optionally dissolved in a suitable organic solvent, with acetylene in the presence of a supported platinum metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands selected from the group consisting of triphenylphosphine, and 1,2-diphenylphosphinobenzene (1,2-DPPB), or optionally in the presence of one or more additives selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate, and tributylamine, or mixtures thereof; wherein reaction temperature and pressure, the catalyst and optionally the ligand(s) and additive(s) are selected such that the Relative Activity is at least 100.

12. The process according to Claim 11, wherein said carboxylic acid is benzoic acid.

13. The process according to Claim 11, wherein said carboxylic acid is 2-ethylhexanoic acid.

14. The process according to Claim 11, wherein the catalyst support is carbon, activated carbon, alumina or titania.

15. The process according to Claim 11, wherein the loading level of the metal is from about 0.1 weight percent to about 10 weight percent.

16. The process according to Claim 11, wherein the carboxylic acid and catalyst are provided in a molar acid:metal ratio of from about 3000:1 to about 380:1.

17. The process according to Claim 11, wherein the reaction temperature ranges from about 50°C to about 180°C.

18. A heterogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a supported platinum catalyst and optionally in the presence of triphenylphosphine as a ligand, and optionally an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine, wherein the platinum loading of the catalyst is from about 0.5 weight % up to about 10 weight %, the support is selected from carbon, activated carbon, titania, alumina, or zirconia, and the benzoic acid is provided in a molar ratio of benzoic acid:platinum metal of about 300:1 to about 4000:1.

19. The process according to Claim 18, wherein the catalyst support is carbon, activated carbon, or titania.

20. The process according to Claim 18, wherein the reaction temperature ranges from about 100°C to about 180°C.

21. A heterogeneous process for the selective formation of vinyl 2-ethylhexanoate from 2-ethylhexanoic acid which comprises reacting 2-ethylhexanoic acid with acetylene, optionally in a suitable organic solvent, at a suitable temperature and pressure in the presence of a supported platinum catalyst, optionally in the presence of triphenylphosphine as a ligand, and optionally in the presence of an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine, wherein the platinum loading of the catalyst is from about 0.5 weight % up to about 10 weight %, the support is selected from carbon, activated carbon, titania, alumina, or zirconia, and the 2-ethylhexanoic acid is provided in a molar ratio of 2-ethylhexanoic acid:platinum metal of about 300:1 to about 4000:1.

22. The process according to Claim 21, wherein the reaction temperature ranges from about 140°C to about 200°C.

23. The process according to Claim 21, wherein the support is carbon or activated carbon and wherein the platinum is present at a loading level of from about 0.5 weight percent to about 6 weight percent.

24. The process according to Claim 21, wherein the support is carbon and the ligand is triphenylphosphine.

25. The process according to Claim 21, wherein the supported platinum catalyst is 0.5 weight percent platinum supported on carbon.

26. The process according to Claim 21, wherein the supported platinum catalyst is one (1) weight percent platinum supported on carbon.

27. The process according to Claim 21, wherein the supported platinum catalyst is three (3) weight percent platinum supported on carbon.

28. The process according to Claim 21, wherein the supported platinum catalyst is a combination of palladium and platinum and the support is carbon, and wherein the palladium and platinum are present at a loading level of from about 1 weight percent to about 5 weight percent.

29. The process according to Claim 21, wherein the supported platinum catalyst is one (1) weight percent platinum on carbon and the reaction temperature is about 160°C.

30. A heterogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a temperature in the range of about 100°C to about 180°C in the presence of a supported platinum catalyst chosen from 1% platinum on carbon, 3% platinum on activated carbon, 5% platinum on titania or 0.5% platinum on alumina and optionally in the presence of triphenylphosphine as a ligand, and optionally an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine.

31. The process according to Claim 30, wherein the reaction temperature ranges from about 110°C to about 170°C.

32. The process according to Claim 30, wherein the reaction temperature ranges from about 120°C to about 160°C.

33. The process according to Claim 30, wherein the supported metal catalyst is five (5) weight percent platinum supported on titania.

34. The process according to Claim 30, wherein the selectivity to vinyl ester based on carboxylic acid consumed is at least 60 percent.

35. The process according to Claim 1, wherein said ligand is selected from the group consisting of triphenylphosphine, and 1,2-diphenylphosphinobenzene (1,2-DPPB).

36. The process according to Claim 1, wherein said additive is selected from the group consisting of potassium acetate, lithium chloride, sodium benzoate, sodium chloride, sodium iodide, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, and tert-butylammonium acetate.

37. The process according to Claim 11, wherein the Relative Activity is at least 300.

38. The process according to Claim 11, wherein the Relative Activity is at least 500.

39. The process according to Claim 11, wherein the Relative Activity is in the range of from 100 to 800.

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WHAT IS CLAIMED IS:

1. A heterogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally dissolved in a suitable organic solvent, at a suitable temperature and pressure, in the presence of a supported metal catalyst, wherein the catalyst metal is selected from the group consisting of iridium, platinum, and rhodium and is supported on an inorganic support selected from the group consisting of carbon, activated carbon, graphite, silica, titania, alumina, calcium silicate, calcium carbonate, silica-alumina, silica aluminate, zirconia, barium carbonate and barium sulfate;
and wherein further the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid and stearic acid.

2. The process according to Claim 1, wherein the process further comprises the presence of one or more ligands selected from the group consisting of triphenylphosphine and 1,2-diphenylphosphinobenzene (1,2-DPPB).

3. The process according to Claim 1, wherein the process further comprises the presence of one or more additives selected from the group consisting of potassium acetate, lithium chloride, sodium benzoate, sodium chloride, sodium iodide, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, and tert-butylammonium acetate.

4. The process according to Claim 1, wherein the carboxylic acid is dissolved in a suitable organic solvent selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

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10. The process according to Claim 5, wherein the support is carbon or activated carbon and wherein the platinum is present at a loading level of from 0.5 weight percent to 6 weight percent.

11. The process according to Claim 9, wherein the catalyst support is carbon, activated carbon, or titania.

12. The process according to Claim 9, wherein the reaction temperature ranges from 100°C to 180°C.

13. The process according to Claim 9, wherein the reaction temperature ranges from 140°C to 200°C.

14. The process according to Claim 9, wherein the pressure is from 101.325 kilopascals to 202.650 kilopascals.

practice of this invention it is possible to attain a Relative Activity of at least 80 and up to about 2000.

Other aspects and advantages of the present invention are described in the detailed description below and in the claims.

Brief Description of the Drawings:

The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts. In the **Figures:**

Figure 1 is a schematic diagram of an apparatus suitable for producing vinyl ester from a carboxylic acid and acetylene in accordance with the process of the present invention;

Figure 2 is a process flow diagram illustrating one suitable industrial scale system for the production of vinyl ester from a carboxylic acid and acetylene according to this invention;

Figure 3 is an illustration of the relative selectivity to vinyl benzoate achieved using a variety of catalyst metals according to the process of the invention; and

Figure 4 is an illustration of the Relative Activity achieved using a variety of catalyst metals according to the process of the invention.

Detailed Description of the Invention

The invention is described in detail below with reference to several embodiments and numerous examples. Terminology used herein is given its ordinary meaning consistent with the exemplary definitions set forth immediately below.

As used herein, a heterogeneous catalyst refers to a catalyst that is in a different phase than the reactants during catalysis. In order for the reaction to occur, one or more of the reactants must diffuse to the catalyst surface and adsorb

onto it. After reaction, the products must desorb and diffuse away from the surface. In contrast, as used herein a homogeneous catalyst refers to a catalyst that is present in the same phase as the reactants.

Mole percent (mole %) and like terms refer to mole percent unless otherwise indicated. Weight percent (wt % or %) and like terms refer to weight percent unless otherwise indicated.

"Conversion" refers to the fraction of reactant consumed in the reaction and is expressed as a mass percentage based on the amount of carboxylic acid in the feed. The conversion of carboxylic acid (CA) is calculated from gas chromatography (GC) data using the following equation:

$$\text{CA conversion (\%)} = 100 * \frac{\text{mass CA, in - mass CA, out (GC)}}{\text{mass CA, in}}$$

where mass CA, in = mass of carboxylic acid loaded (weighed in) into the reactor, and mass CA, out (GC) = mass of carboxylic acid after the reaction based on GC data.

"Selectivity" refers to the amount of vinyl ester produced relative to the carboxylic acid consumed and is expressed as a mole percent based on converted carboxylic acid. For example, if the conversion is 50 mole % and 50 mole % of the converted carboxylic acid is converted to vinyl ester, we refer to the vinyl

showed that TONs were below 0.1 for most of the catalysts in this group, and none of the TONs exceeded 20.

The invention is defined in the appended claims.

What is claimed is:

1. A heterogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid, optionally dissolved in a suitable organic solvent, with acetylene in the presence of a supported platinum catalyst at a suitable reaction temperature and pressure, wherein the platinum loading of the catalyst is from about 0.1 weight % up to about 10 weight % and the support is selected from carbon, activated carbon, titania, alumina, or zirconia, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

2. The process according to claim **1**, wherein said carboxylic acid is benzoic acid.

3. The process according to claim **1**, wherein said carboxylic acid is 2-ethylhexanoic acid.

4. The process according to claim **1**, wherein the reaction temperature ranges from about 50° C. to about 180° C.

5. A heterogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene at a suitable reaction temperature and pressure in the presence of a supported platinum catalyst without ligand, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

6. The process according to claim **5**, wherein the catalyst support is carbon, activated carbon, or titania.

7. The process according to claim **5**, wherein the reaction temperature ranges from about 100° C. to about 180° C.

8. The process according to claim **5**, wherein the reaction temperature ranges from about 140° C. to about 200° C.

9. The process according to claim **1**, wherein the support is carbon or activated carbon and wherein the platinum is present at a loading level of from about 0.5 weight percent to about 6 weight percent.

10. The process according to claim **1**, wherein the process is further characterized by a selectivity to the vinyl ester of at least 50%.

11. The process according to claim 1, wherein the process is further characterized by a carboxylic acid conversion of at least 50%.

12. The process according to claim 5, wherein the pressure is from about 1 atmosphere absolute to about 2 atmospheres absolute.

13. A heterogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable pressure and temperature, in the presence of a supported metal catalyst, wherein the catalyst metal is selected from the group consisting of iridium, platinum, and rhodium, and is supported on an inorganic support selected from the group consisting of carbon, activated carbon, graphite, silica, titania, alumina, calcium silicate, calcium carbonate, silica-alumina, silica aluminate, zirconia, barium carbonate, and barium sulfate, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

14. The process according to claim 13, wherein the process further comprises the presence of one or more ligands selected from the group consisting of triphenylphosphine and 1,2-diphenylphosphinobenzene (1,2-DPPB).

15. The process according to claim 13, wherein the process further comprises the presence of one or more additives selected from the group consisting of potassium acetate, lithium chloride, sodium benzoate, sodium chloride, sodium iodide, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl) ammonium chloride and tetrabutylammonium acetate.

16. The process according to claim 13, wherein the carboxylic acid is dissolved in a suitable organic solvent selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.