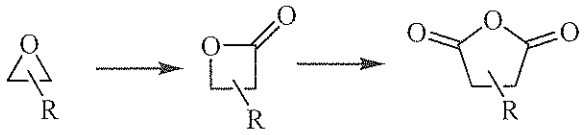
lactones, subsequent carbonylation of these β-lactones constitutes a versatile two-step method for the stereoselective synthesis of succinic anhydrides. (Scheme 1).



Scheme 1

Summary ~~of the Invention~~

In a first aspect of the present disclosure, there is provided a method of synthesizing an acid anhydride comprising the steps of:

a) feeding a reaction stream comprising an epoxide, at least one catalyst, at least one solvent, and carbon monoxide to a reaction vessel under reaction conditions to promote a double carbonylation of the epoxide to form dissolved acid anhydride in the reaction vessel, which exits the reaction vessel in a reaction product stream in a continuous flow process;

b) treating the reaction product stream containing dissolved acid anhydride to conditions that cause the acid anhydride to crystallize such that the reaction product stream comprises crystallized acid anhydride and a liquid phase comprising dissolved catalyst and solvent;

c) separating the crystallized acid anhydride from the liquid phase; and

d) recycling the liquid phase comprising dissolved catalyst and solvent to the reaction stream comprising the epoxide;

wherein the catalyst comprises a transition metal carbonyl compound and further comprises a Lewis acidic co-catalyst.

TIn various aspects, the present inventiondisclosure includes a method of synthesizing succinic anhydride including the steps of: feeding a reaction stream including ethylene oxide, at least one catalyst, at least one solvent, and carbon monoxide to a reaction vessel under reaction conditions to promote a double carbonylation of ethylene oxide to form succinic anhydride in the reaction stream in a continuous flow process; b) treating the reaction stream containing succinic anhydride to conditions that cause the succinic anhydride to crystallize such that the reaction stream includes crystallized succinic anhydride and a liquid phase including catalyst and solvent; c) separating the crystallized succinic anhydride from the liquid phase; and d) recycling the catalyst and the solvent to the reaction stream including the ethylene oxide.

In some embodiments, the solvent includes dioxane. In some embodiments, step b) occurs in an adiabatic evaporative cooling crystallizer. In some embodiments, step c) occurs in a rotary drum filter. In some embodiments, step d) includes the substep of feeding a solution including the catalyst and the solvent to a recovery flash drum to separate volatiles prior to returning the solution to the reaction stream. In some embodiments, the method further includes treating the solution by performing at least one step selected from the group consisting of: drying the solution; heating or cooling the solution; removing spent catalyst; adding solvent; and any combination of two or more of these.

In some embodiments, the first carbonylation reaction is performed at a pressure from about 50 psi to about 5000 psi. In some embodiments, the first carbonylation reaction is

some embodiments, M' is selected from the group consisting of: a transition metal, a group 13 or 14 metal, and a lanthanide. In some embodiments, M' is a transition metal or a group 13 metal. In some embodiments, M' is selected from the group consisting of aluminum, chromium, indium and gallium. In some embodiments, M' is aluminum. In some embodiments, M' is chromium.

In some embodiments, the Lewis acid includes a dianionic tetradentate ligand. In some embodiments, the dianionic tetradentate ligand is selected from the group consisting of: porphyrin derivatives; salen derivatives; dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives; phthalocyaninate derivatives; and derivatives of the Trost ligand. In some embodiments step c) includes the substep of filtering the reaction stream.

TIn various aspects, the present inventiondisclosure provides a succinic anhydride synthesis system including: a carbon monoxide source; an ethylene oxide source; a solvent source; a catalyst source; at least one reaction vessel fed with a reaction stream by the carbon monoxide source, the ethylene oxide source, the solvent source, and the catalyst source, the reaction stream including carbon monoxide, ethylene oxide, solvent, and catalyst; an adiabatic evaporative cooling crystallizer fed from the at least one reaction vessel; a rotary drum filter fed by the adiabatic evaporative cooling crystallizer; a solids dryer fed by the rotary drum filter; and a recovery flash drum fed by the adiabatic evaporative cooling crystallizer, the rotary drum filter, and the solids dryer, the recovery flash drum feeding recycled catalyst and solvent to the reaction stream.

In some embodiments, the reaction vessel includes a tubular reactor. In some embodiments, the reaction vessel includes a shell and tube adiabatic reactor. In some embodiments, the adiabatic evaporative cooling crystallizer includes a feed cooler and a crystallizer flash drum.

In some embodiments, the carbon monoxide source includes: a methane source; a steam reforming unit fed by the methane source; a hydrogen pressure swing adsorption unit fed by the steam reforming unit; a carbon monoxide pressure swing adsorption unit fed by the hydrogen pressure swing adsorption unit; a carbon monoxide compressor fed by the carbon

REPLACEMENT SHEET

Claims

What is claimed is:

1. A method of synthesizing an acid anhydride comprising the steps of:

a) feeding a reaction stream comprising an epoxide, at least one catalyst, at least one solvent, and carbon monoxide to a reaction vessel under reaction conditions to promote a double carbonylation of the epoxide to form ~~an~~ dissolved acid anhydride in the reaction vessel, which exits the reaction vessel in a reaction product stream in a continuous flow process;

b) treating the reaction product stream containing dissolved acid anhydride to conditions that cause the acid anhydride to crystallize such that the reaction product stream comprises crystallized acid anhydride and a liquid phase comprising dissolved catalyst and solvent;

c) separating the crystallized acid anhydride from the liquid phase; and

d) recycling the liquid phase comprising dissolved catalyst and solvent to the reaction stream comprising the epoxide.

2. The method of claim 1, wherein step b) occurs in an adiabatic evaporative cooling crystallizer.

3. The method of claim 1, wherein step c) occurs in a rotary drum filter.

4. The method of claim 1, wherein step d) comprises feeding the liquid phase comprising dissolved catalyst and solvent to a recovery flash drum to separate volatiles prior to returning it to the reaction stream.

5. The method of claim 4, further comprising treating the liquid phase by performing at least one step selected from the group consisting of: drying; heating or cooling; removing spent catalyst; adding solvent; and any combination of two or more of these.

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6. The method of any one of claims 1 to 5, wherein the epoxide is selected from the group consisting of ethylene oxide, propylene oxide, epichlorohydrin, 1,2-butylene oxide, 2,4 butylene oxide, and an oxide of C_{5-30} alpha olefin.

7. The method of claim 6, wherein the epoxide is ethylene epoxide.

8. The method of any one of claims 1 to 5, wherein the acid anhydride is selected from the group consisting of succinic anhydride, methylsuccinic anhydride, chloromethylsuccinic anhydride, ethylsuccinic anhydride, or C_{5-30} acid anhydrides.

9. The method of claim 8 wherein the acid anhydride is succinic anhydride.

10. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 50 psi to about 5000 psi.

11. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 50 psi to about 2000 psi.

12. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 200 psi to about 1000 psi.

13. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 200 psi to about 600 psi.

14. The method of claim 1, wherein the first carbonylation reaction is performed at a temperature from about 0 °C to about 125 °C

15. The method of claim 1, wherein the first carbonylation reaction is performed at a temperature from about 30 °C to about 100 °C.

16. The method of claim 1, wherein the first carbonylation reaction is performed at a temperature from about 40 °C to about 80 °C.

17. The method of any one of the preceding claims, wherein the reaction is operated under steady state reaction conditions.

18. The method of any one of claims 1 to 16, wherein the reaction is operated under steady state reaction conditions.

19. The method of any one of the preceding claims, wherein the double carbonylation is performed in one or more continuous stirred tank reactors.

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20. The method of any one of the preceding claims, wherein the double carbonylation is performed in one or more plug flow reactors.

21. The method of any one of the preceding claims, wherein the double carbonylation reaction is performed in an adiabatic reactor.

22. The method of claim 21, wherein the adiabatic reactor is a tubular reactor.

23. The method of claim 21, wherein the adiabatic reactor is a shell and tube reactor.

24. The method of claim 1, wherein the solvent is selected from the group consisting of 1,4-dioxane; 1,3-dioxane; tetrahydrofuran; tetrahydropyran; dimethoxyethane; glyme; diethyl ether; t-butyl methyl ether; 2,5-dimethyl tetrahydrofuran; ethyl acetate; propyl acetate; butyl acetate; acetone; 2-butanone; cyclohexanone; toluene; acetonitrile; difluorobenzene and combinations thereof.

25. The method of claim 24, wherein the solvent comprises 1,4-dioxane.

26. The method of claim 1, wherein the at least one catalyst is a single catalyst.

27. The method of claim 26, wherein the single catalyst is $[(ClTPP)Al(THF)_2]^+[Co(CO)_4]^-$, wherein ClTPP is *meso*-tetra(4-chlorophenyl)porphyrinato and THF is tetrahydrofuran.

28. The method of claim 1, wherein the at least one catalyst comprises a first catalyst selected to promote a first carbonylation of the double carbonylation and a second catalyst different from the first catalyst selected to promote a second carbonylation of the double carbonylation.

29. The method of claim 1, wherein the catalyst comprises a metal carbonyl compound.

30. The method of claim 29, wherein the metal carbonyl compound has the formula $[QM_y(CO)_w]^{x-}$, where:

Q is any ligand and need not be present;

M is a metal atom;

y is an integer from 1 to 6 inclusive;

w is a number such as to provide the stable metal carbonyl; and

x is an integer from -3 to +3 inclusive.

31. The method of claim 30, wherein M is selected from the group consisting of Ti, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Cu, Zn, Al, Ga, and In.

32. The method of claim 30, wherein M is Co.

33. The method of claim 30, wherein the carbonylation catalyst further comprises a Lewis acidic co-catalyst.

34. The method of claim 33, wherein the metal carbonyl compound is anionic, and the Lewis acidic co-catalyst is cationic.

35. The method of claim 34, wherein the metal carbonyl complex comprises a carbonyl cobaltate and the Lewis acidic co-catalyst comprises a metal-centered Lewis acid.

36. The method of claim 35, wherein the metal-centered Lewis acid is a metal complex of formula $[M'(L)_b]^{c-}$, where:

M' is a metal;

each L is a ligand;

b is an integer from 1 to 6 inclusive;

c is 1, 2, or 3; and

where, if more than one L is present, each L may be the same or different.

37. The method of claim 36, wherein M' is selected from the group consisting of: a transition metal, a group 13 or 14 metal, and a lanthanide.

38. The method of claim 36, wherein M' is a transition metal or a group 13 metal.

39. The method of claim 36, wherein M' is selected from the group consisting of aluminum, chromium, indium and gallium.

40. The method of claim 36, wherein M' is aluminum.

41. The method of claim 36, wherein M' is chromium.

42. The method of claim 36, wherein the Lewis acid includes a dianionic tetradentate ligand.

43. The method of claim 42, wherein the dianionic tetradentate ligand is selected from the group consisting of: porphyrin derivatives; salen derivatives; dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives; phthalocyaninate derivatives; and derivatives of the Trost ligand.

44. The method of claim 1, wherein step c) comprises filtering the reaction product stream.

45. A succinic anhydride synthesis system comprising:

a carbon monoxide source;

an ethylene oxide source;

a solvent source;

a catalyst source;

at least one reaction vessel fed with a reaction stream by the carbon monoxide source, the ethylene oxide source, the solvent source, and the catalyst source, the reaction stream comprising carbon monoxide, ethylene oxide, solvent, and catalyst;

an adiabatic evaporative cooling crystallizer fed from the at least one reaction vessel;

a rotary drum filter fed by the adiabatic evaporative cooling crystallizer; and

a solids dryer fed by the rotary drum filter.

46. The synthesis system of claim 45, wherein the reaction vessel comprises a tubular reactor.

47. The synthesis system of claim 45, wherein the reaction vessel comprises a shell and tube adiabatic reactor.

48. The synthesis system of claim 45, wherein the adiabatic evaporative cooling crystallizer comprises a feed cooler and a crystallizer flash drum.

49. The synthesis system of claim 45, wherein the carbon monoxide source comprises:

a methane source;

a steam reforming unit fed by the methane source;

a hydrogen pressure swing adsorption unit fed by the steam reforming unit;

a carbon monoxide pressure swing adsorption unit fed by the hydrogen pressure swing adsorption unit;

a carbon monoxide compressor fed by the carbon monoxide pressure swing adsorption unit; and

a carbon monoxide dryer fed by the carbon monoxide compressor.

50. The synthesis system of claim 45, wherein the solvent source comprises:

a solvent offloading pump;

a solvent dryer fed by the solvent offloading pump; and

a solvent storage tank fed by the solvent dryer; and

a solvent charge pump fed by the solvent storage tank.

51. The synthesis system of claim 45, wherein the catalyst source comprises a catalyst mix tank and a catalyst charge pump fed by the catalyst mix tank, wherein the solvent charge pump feeds solvent to the catalyst mix tank.

Claims

What is claimed is:

1. A method of synthesizing an acid anhydride comprising the steps of:

a) feeding a reaction stream comprising an epoxide, at least one catalyst, at least one solvent, and carbon monoxide to a reaction vessel under reaction conditions to promote a double carbonylation of the epoxide to form dissolved acid anhydride in the reaction vessel, which exits the reaction vessel in a reaction product stream in a continuous flow process;

b) treating the reaction product stream containing dissolved acid anhydride to conditions that cause the acid anhydride to crystallize such that the reaction product stream comprises crystallized acid anhydride and a liquid phase comprising dissolved catalyst and solvent;

c) separating the crystallized acid anhydride from the liquid phase; and

d) recycling the liquid phase comprising dissolved catalyst and solvent to the reaction stream comprising the epoxide;

wherein the catalyst comprises a transition metal carbonyl compound and further comprises a Lewis acidic co-catalyst.

2. The method of claim 1, wherein step b) occurs in an adiabatic evaporative cooling crystallizer.

3. The method of claim 1, wherein step c) occurs in a rotary drum filter.

4. The method of claim 1, wherein step d) comprises feeding the liquid phase comprising dissolved catalyst and solvent to a recovery flash drum to separate volatiles prior to returning it to the reaction stream.

5. The method of claim 4, further comprising treating the liquid phase by performing at least one step selected from the group consisting of: drying; heating or cooling; removing spent catalyst; adding solvent; and any combination of two or more of these.

6. The method of claim 1, wherein the epoxide is selected from the group consisting of ethylene oxide, propylene oxide, epichlorohydrin, 1,2-butylene oxide, 2,4 butylene oxide, and an oxide of C_{5-30} alpha olefin.

7. The method of claim 6, wherein the epoxide is ethylene oxide.

8. The method of claim 1, wherein the acid anhydride is selected from the group consisting of succinic anhydride, methylsuccinic anhydride, chloromethylsuccinic anhydride, ethylsuccinic anhydride, and C_{5-30} acid anhydrides.

9. The method of claim 8 wherein the acid anhydride is succinic anhydride.

10. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 50 psi to about 5000 psi.

11. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 50 psi to about 2000 psi.

12. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 200 psi to about 1000 psi.

13. The method of claim 1, wherein the first carbonylation reaction is performed at a pressure from about 200 psi to about 600 psi.

14. The method of claim 1, wherein the first carbonylation reaction is performed at a temperature from about 0 °C to about 125 °C

15. The method of claim 1, wherein the first carbonylation reaction is performed at a temperature from about 30 °C to about 100 °C.

16. The method of claim 1, wherein the first carbonylation reaction is performed at a temperature from about 40 °C to about 80 °C.

17. The method of claim 1, wherein the reaction is operated under steady state reaction conditions.

18. The method of claim 1, wherein the double carbonylation is performed in one or more continuous stirred tank reactors.

19. The method of claim 1, wherein the double carbonylation is performed in one or more plug flow reactors.

20. The method of any one of the preceding claims, wherein the double carbonylation reaction is performed in an adiabatic reactor.

21. The method of claim 20, wherein the adiabatic reactor is a tubular reactor.

22. The method of claim 20, wherein the adiabatic reactor is a shell and tube reactor.

23. The method of claim 1, wherein the solvent is selected from the group consisting of 1,4-dioxane; 1,3-dioxane; tetrahydrofuran; tetrahydropyran; dimethoxyethane; glyme; diethyl ether; t-butyl methyl ether; 2,5-dimethyl tetrahydrofuran; ethyl acetate; propyl acetate; butyl acetate; acetone; 2-butanone; cyclohexanone; toluene; acetonitrile; difluorobenzene and combinations thereof.

24. The method of claim 23, wherein the solvent comprises 1,4-dioxane.

25. The method of claim 1, wherein the at least one catalyst is a single catalyst.

26. The method of claim 25, wherein the single catalyst is $[(ClTPP)Al(THF)_2]^+[Co(CO)_4]^-$, wherein ClTPP is *meso*-tetra(4-chlorophenyl)porphyrinato and THF is tetrahydrofuran.

27. The method of claim 1, wherein the at least one catalyst comprises a first catalyst selected to promote a first carbonylation of the double carbonylation and a second catalyst different from the first catalyst selected to promote a second carbonylation of the double carbonylation.

28. The method of claim 1, wherein the transition metal carbonyl compound comprises a compound of formula $[M_y(CO)_w]^{x-}$, where:

M is a transition metal atom

y is an integer from 1 to 6 inclusive;

w is a number such as to provide the stable metal carbonyl; and

x is an integer from -3 to +3 inclusive.

29. The method of claim 28, wherein M is selected from the group consisting of Ti, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Cu and Zn.

30. The method of claim 28, wherein M is Co.

31. The method of claim 28, wherein the transition metal carbonyl compound is anionic, and the Lewis acidic co-catalyst is cationic.

32. The method of claim 31, wherein the transition metal carbonyl compound comprises a carbonyl cobaltate and the Lewis acidic co-catalyst comprises a metal-centered Lewis acid.

33. The method of claim 32, wherein the metal-centered Lewis acid is a metal complex of formula $[M'(L)_b]^{c+}$, where:

M' is a metal selected from the group consisting of: a transition metal, a group 13 or 14 metal, and a lanthanide;

each L is a dianionic tetradentate ligand;

b is an integer from 1 to 6 inclusive;

c is 1, 2, or 3; and

where, if more than one L is present, each L may be the same or different.

34. The method of claim 33, wherein M' is selected from the group consisting of: a transition metal, a group 13 or 14 metal, and a lanthanide.

35. The method of claim 33, wherein M' is selected from the group consisting of aluminum, chromium, indium and gallium.

36. The method of claim 33, wherein M' is aluminum.

37. The method of claim 33, wherein M' is chromium.

38. The method of claim 33, wherein the dianionic tetradentate ligand is a ligand comprising a porphyrin; salen; dibenzotetramethyltetraaza[14]annulene (tmtaa); phthalocyaninate; or Trost ligand.

39. The method of claim 1, wherein step c) comprises filtering the reaction product stream.