[0009] U.S. Patent No. 4,400,468 discloses a process for producing adipic acid from a renewable resource, specifically, biomass such as waste material selected from paper, wood, cornstalks and logging residue. The process involves oxidizing 1,6-hexanediol in the presence of a microorganism, such as *Gluconobacter oxydans* subsp. *oxydans*, to produce adipic acid. No examples are disclosed in this patent regarding any yields obtainable from this process.

[0010] In light of the changing environment toward utilization of cheaper, renewable feedstocks, the discovery of new, industrially scalable methods for the selective and economical production of adipic acid from 1,6-hexanediol could have extraordinary value in the near future.

SUMMARY

[0011] The present ~~invention~~ disclosure is directed to processes for preparing adipic acid from 1,6-hexanediol, which may be obtained from renewable materials. Generally, the process for preparing adipic acid from 1,6-hexanediol includes chemocatalytically converting 1,6-hexanediol to the adipic acid product in the presence of oxygen and a heterogeneous catalyst that may include platinum and/or gold.

[0011a] In a first aspect of the present disclosure, there is provided a process for preparing an adipic acid product, the process comprising chemocatically converting 1,6-hexanediol to the adipic acid product by a method comprising reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst comprising at least one metal selected from the group consisting of gold and platinum.

[0011b] In a second aspect of the present disclosure, there is provided a process for preparing an adipic acid product, the process comprising reacting 1,6-hexanediol with oxygen in the presence of a catalyst comprising platinum on a zirconia or stabilized zirconia support.

[0011c] In a third aspect of the present disclosure, there is provided a catalyst comprising at least one metal selected from the group consisting of gold and platinum, wherein the at least one metal is on a support, wherein at least the outer surfaces of the support are zirconia or stabilized zirconia, wherein the surface area of the support is equal to or less than about 100 m2/g and the average pore diameter is at least about 10 nm, and wherein the ziroconia or stabilized zirconia comprises tungsten in an amount ranging from about 1 wt% to about 15wt% of the total weight of the support.

[0012] ~~In one aspect,~~There is provided ~~is~~ a process for preparing adipic acid product, by: reacting 1,6-hexanediol and oxygen in the presence of a catalyst that includes platinum on a zirconia or stabilized zirconia support. In some embodiments, the heterogeneous catalyst has a support, in which the outer surfaces of the support are made up of a material selected from zirconia, stabilized zirconia, zirconia-metal or - metal oxide composites, titania, stabilized titania, titania-metal or - metal oxide composites, silica and mixtures thereof. In certain embodiments, the surface area of the support is equal to or less than about $220m^2/g$ and the average pore diameter is at least about 5 nm. In certain embodiments, the support further includes tungsten.

[0013] In other embodiments, the heterogeneous catalyst includes a support selected form zirconia, stabilized zirconia, stabilized zirconia- metal or - metal oxide composite, titania, stabilized titania, stabilized titania-metal or – metal oxide composite, and mixtures thereof. In certain embodiments, the support is selected from stabilized zirconia, stabilized titania, and mixtures thereof, and the support contains tungsten. In certain embodiments, the tungsten is present in an amount ranging from about 1 wt% to about 15 wt% of the total weight of the support. In yet other embodiments, the support has a surface equal to or less than about $220m^2/g$ and an average pore diameter of at least about 5 nm. In one embodiment, the support has a surface equal to or less than about $100m^2/g$ and an average pore diameter of at least about 10 nm.

CLAIMS

We claim:

1. A process for preparing an adipic acid product, the process comprising chemocatalytically converting 1,6-hexanediol to the adipic acid product, wherein the step of chemocatalytically converting 1,6-hexanediol to the adipic acid product comprises reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst comprising at least one metal selected from the group consisting of gold and platinum.

2. A process for preparing adipic acid product, the process comprising: reacting 1,6-hexanediol and oxygen in the presence of a catalyst comprising platinum on a zirconia or stabilized zirconia support.

3. The process of claim 1 wherein the heterogeneous catalyst comprises a support, wherein the outer surfaces of the support are a material selected from the group consisting of zirconia, stabilized zirconia, zirconia-metal or -metal oxide composites, titania, stabilized titania, titania-metal or - metal oxide composites, silica and mixtures thereof.

4. The process of claim 2 wherein the surface area of the support is equal to or less than about 220m^2/g and the average pore diameter is at least about 5 nm.

5. The process of claim 2 or 4 wherein the support further comprises tungsten.

6. The process of claim 1 wherein the heterogeneous catalyst comprises a support selected form the group consisting of zirconia, stabilized zirconia, stabilized zirconia- metal or -metal oxide composite, titania, stabilized titania, stabilized titania-metal or -metal oxide composite, and mixtures thereof.

7. The process of claim 3 or 6, wherein the support is selected from the group consisting of stabilized zirconia, stabilized titania, and mixtures thereof, and the support contains tungsten.

8. The process of claim 5 or 7 wherein the tungsten is present in an amount ranging from about 1 wt% to about 15 wt% of the total weight of the support.

9. The process of any one of claims 3 and 6 to 8 wherein the support has a surface equal to or less than about 220m^2/g and an average pore diameter of at least about 5 nm.

10. The process of any one of claims 3 and 6 to 8 wherein the support has a surface equal to or less than about 100m^2/g and an average pore diameter of at least about 10 nm.

11. The process of any one of claims 1 to 10, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst comprises:

a) combining the 1,6-hexanediol and the heterogeneous catalyst, and optionally a solvent; and

b) contacting the combined 1,6-hexanediol and heterogeneous catalyst, and optionally the solvent, with oxygen.

12. The process of any one of claims 1 to 10, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst and, optionally a solvent comprises:

a) combining the 1,6-hexanediol and the heterogeneous catalyst, and optionally a solvent, at a temperature equal to or less than about 120°C ; and

b) contacting with oxygen the combined 1,6-hexanediol and heterogeneous catalyst, and optionally the solvent.

13. The process of any one of claims 1 to 10, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst comprises:

a) combining the 1,6-hexanediol and a solvent;

b) contacting the combined 1,6-hexanediol and solvent with a heterogeneous catalyst; and

c) contacting the combined 1,6-hexanediol, solvent, and heterogeneous catalyst with oxygen.

14. The process of any one of claims 10 to 13, wherein the solvent is selected from the group consisting of water, alcohols, ethers, and mixtures thereof.

15. The process of claim 1 or 2, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst and water comprises:

a) contacting the 1,6-hexanediol with water;

b) contacting the 1,6-hexanediol and water with the heterogeneous catalyst; and,

c) contacting the combined 1,6-hexanediol, water, and heterogeneous catalyst with oxygen.

16. The process of any one of claims 1 to 15, wherein the 1,6-hexanediol is derived from a carbohydrate source.

17. The process of any one of claims 1 to 16, wherein the reaction is conducted under a partial pressure of oxygen ranging from about 50 psi to about 2000 psi.

18. The process of any one of claims 1 to 16, wherein the partial pressure of oxygen ranges from about 50 psig to about 1000 psig.

19. The process of any one of claims 1 to 16, wherein the partial pressure of oxygen ranges from about 50 psig to about 700 psig.

20. The process of any one of claims 1 to 19, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature ranging from about 100°C to about 180°C.

21. The process of any one of claims 1 to 19, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature ranging from about 135°C to about 165°C.

22. The process of any one of claims 1 to 21, wherein the adipic acid product is produced in at least about 80% yield from the 1,6-hexanediol.

23. The process of any one of claims 1 to 22, wherein the adipic acid product is produced in at least about 90% yield from the 1,6-hexanediol.

24. The process of any one of claims 1 to 23 wherein the catalyst further comprises palladium.

25. The process of any one of claims 1 to 24 wherein gold is present in an amount up to about 4 wt% of the total catalyst weight.

26. The process of any one of claims 1 to 25 wherein platinum is present in an amount up to about 4 wt% of the total catalyst weight.

27. The process of any one of claims 1 to 24 wherein the catalyst comprises gold and platinum and the gold and platinum are present in an amount, in sum, up to about 4 wt% of the total catalyst weight.

28. A catalyst comprising at least one metal selected from the group consisting of gold and platinum, wherein the at least one metal is on a support, wherein at least the outer surfaces of the support are zirconia or stabilized zirconia, wherein the surface area of the support is equal to or less than about $100 m^2/g$ and the average pore diameter is at least about 10 nm, and wherein the zirconia or stabilized zirconia comprises tungsten in an amount ranging from about 1 wt% to about 15 wt% of the total weight of the support.

29. The catalyst of claim 28 wherein the outer surfaces consist essentially of stabilized zirconia.

30. The catalyst of claim 28 or 29 wherein the catalyst consists essentially of platinum on such support.

31. The catalyst of claim 28 or 29 wherein the catalyst consists essentially of platinum and gold on such support.

32. The catalyst of claim 28 or 29 wherein the catalyst further comprises palladium.

33. The catalyst of any one of claims 28 to 33 wherein the at least one metal is present, in sum, in an amount up to about 4 wt% of the total weight of the catalyst.

CLAIMS

We claim:

1. A process for preparing an adipic acid product, the process comprising chemocatically converting 1,6-hexanediol to the adipic acid product by a method comprising reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst comprising at least one metal selected from the group consisting of gold and platinum.

2. The process of claim 1, wherein the catalyst comprises gold.

3. The process of claim 1, wherein the catalyst comprises platinum.

4. The process of claim 1, wherein the catalyst comprises gold and platinum.

5. The process of any one of claims 1-4, wherein the weight percent of gold to the total weight of the finished catalyst is from about 0.1 wt% to about 10 wt%.

6. A process for preparing an adipic acid product, the process comprising reacting 1,6-hexanediol with oxygen in the presence of a catalyst comprising platinum on a zirconia or stabilized zirconia support.

7. The process of any one of claims 1-5, wherein the heterogeneous catalyst comprises a support, wherein the outer surfaces of the support comprise a material selected from the group consisting of zirconia, stabilized zirconia, zirconia-metal or zirconia–metal oxide composites, titania, stabilized titania, titania-metal or titania–metal oxide composites, alumina, silica and mixtures thereof.

8. The process of claim 6, wherein the surface area of the support is equal to or less than about $220 m^2/g$ and the average pore diameter is at least about 5 nm.

9. The process of any one of claims 6 or 8, wherein the support further comprises tungsten.

10. The process of any one of claims 1-5, wherein the heterogeneous catalyst comprises a support selected from the group consisting of zirconia, stabilized zirconia, stabilized zirconia- metal or zirconia–metal oxide composite, titania, stabilized titania, stabilized titania-metal or titania–metal oxide composite, and mixtures thereof.

11. The process of claim 7 or 10, wherein the support is selected from the group consisting of stabilized zirconia, stabilized titania, and mixtures thereof, and the support contains tungsten.

12. The process of claim 9 or 11, wherein the tungsten is present in an amount ranging from about 1 wt% to about 15% of the total weight of the support.

13. The process of any one of claims 7 and 10 to 12, wherein the support has a surface area equal to or less than about 220m^2/g and an average pore diameter of at least about 5 nm.

14. The process of any one of claims 7 and 10 to 12, wherein the support has a surface area equal to or less than about 100m^2/g and an average pore diameter of at least about 10 nm.

15. The process of any one of claims 1 to 14, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst comprises:

a) combining the 1,6-hexanediol and the heterogeneous catalyst, and optionally a solvent; and

b) contacting the combined 1,6-hexanediol and heterogeneous catalyst and optionally the solvent, with oxygen.

16. The process of any one of claims 1 to 14, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst and, optionally a solvent comprises:

a) combining the 1,6-hexanediol and the heterogeneous catalyst, and optionally a solvent, at a temperature equal to or less than about 120°C ; and

b) contacting with oxygen the combined 1,6-hexanediol and heterogeneous catalyst, and optionally the solvent.

17. The process of any one of claims 1 to 14, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst comprises:

a) combining the 1,6-hexanediol and a solvent;

b) contacting the combined 1,6-hexanediol and solvent with a heterogeneous catalyst; and

c) contacting the combined 1,6-hexanediol, solvent, and heterogeneous catalyst with oxygen.

18. The process of any one of claims 15 to 17, wherein the solvent is selected from the group consisting of water, alcohols, ethers, and mixtures thereof.

19. The process of any one of claims 1-14, wherein reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst comprises:

a) contacting the 1,6-hexanediol with water;

b) contacting the 1,6-hexanediol and water with the heterogeneous catalyst; and,

c) contacting the combined 1,6-hexanediol, water, and heterogeneous catalyst with oxygen.

20. The process of any one of claims 1 to 19, wherein the 1,6-hexanediol is derived from a carbohydrate source.

21. The process of any one of claims 1 to 20, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out under a partial pressure of oxygen ranging from about 50 psig to about 2000 psig.

22. The process of any one of claims 1 to 20, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out under a partial pressure of oxygen ranging from about 50 psig to about 1000 psig.

23. The process of any one of claims 1 to 2, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out under a partial pressure of oxygen ranging from about 50 psig to about 700 psig.

24. The process of any one of claims 1 to 23, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature ranging from about 100°C to about 180°C.

25. The process of any one of claims 1 to 23, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature ranging from about 135°C to about 165°C.

26. The process of any one of claims 1 to 25, wherein the adipic acid product is produced in at least about 80% yield from the 1,6-hexanediol.

27. The process of any one of claims 1 to 26, wherein the adipic acid product is produced in at least about 90% yield from the 1,6-hexanediol.

28. The process of any one of claims 1 to 27, wherein the catalyst further comprises palladium.

29. The process of any one of claims 1 to 28, wherein gold is present in an amount up to about 4 wt% of the total catalyst weight.

30. The process of any one of claims 1 to 29, wherein platinum is present in an amount up to about 4 wt% of the total catalyst weight.

31. The process of any one of claims 1 to 28, wherein the catalyst comprises gold and platinum and the gold and platinum are present in an amount, in sum, up to about 4 wt% of the total catalyst weight.

32. A catalyst comprising at least one metal selected from the group consisting of gold and platinum, wherein the at least one metal is on a support, wherein at least the outer surfaces of the support are zirconia or stabilized zirconia, wherein the surface area of the support is equal to or less than about 100 m2/g and the average pore diameter is at least about 10 nm, and

wherein the ziroconia or stabilized zirconia comprises tungsten in an amount ranging from about 1 wt% to about 15wt% of the total weight of the support.

33. The catalyst of claim 32, wherein the outer surfaces consist essentially of stabilized zirconia.

34. The catalyst of claim 32 or 33, wherein the catalyst consists essentially of platinum on the support.

35. The catalyst of claim 32 or 33, wherein the catalyst consists essentially of platinum and gold on the support.

36. The catalyst of claim 32 or 33, wherein the catalyst further comprises palladium.

37. The catalyst of any one of claims 32 to 36, wherein the at least one metal is present, in sum, in an amount up to about 4 wt% of the total weight of the catalyst.