[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 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.

[0012] The present disclosure provides 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 examples, 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 examples, 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 examples, the support further includes tungsten.

[0012a] In one aspect of the present disclosure, there is provided a process for preparing adipic acid, the process comprising reacting 1,6-hexanediol and oxygen in the presence of a catalyst comprising platinum on a support comprising zirconia or stabilized zirconia thereby producing a reaction mixture comprising adipic acid, wherein the catalyst does not include gold.

[0013] In other examples, 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 examples, the support is selected from stabilized zirconia, stabilized titania, and mixtures thereof, and the support contains tungsten. In certain examples, 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 examples, the support has a surface equal to or less than about $220 m^2/g$ and an average pore diameter of at least about 5 nm. In one example, the support has a surface equal to or less than about $100 m^2/g$ and an average pore diameter of at least about 10 nm.

[0014] In some examples, reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst includes: 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. In certain examples, reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst, and optionally a solvent includes: 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.

[0015] In other examples, reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst includes: 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. In certain examples, the solvent is selected from water, alcohols, ethers, and mixtures thereof.

[0016] In yet other examples, reacting the 1,6-hexanediol with oxygen in the presence of the heterogeneous catalyst and water includes: 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.

[0017] In some examples, the 1,6-hexanediol is derived from a carbohydrate source. In some examples, the reaction is conducted under a partial pressure of oxygen ranging from about 50 psi to about 2000 psi. In certain examples, the partial pressure of oxygen ranges from about 50 psig to about 1000 psig. In one examnple, the partial pressure of oxygen ranges from about 50 psig to about 700 psig. In other examples, 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. In certain examples, 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. In some examples, the adipic acid product is produced in at least about 80% yield from the 1,6-hexanediol. In one example, the adipic acid product is produced in at least about 90% yield from the 1,6-hexanediol.

[0018] In some examples, the catalyst further includes palladium. In other examples, gold is present in an amount up to about 4 wt% of the total catalyst weight. In yet other examples, platinum is present in an amount up to about 4 wt% of the total catalyst weight.

In certain examples, the catalyst includes 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.

[0019] Provided is also a catalyst that includes at least one metal selected from gold and platinum, in which the at least one metal is on a support, in which at least the outer surfaces of the support are made up of 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 includes tungsten in an amount ranging from about 1 wt% to about 15 wt% of the total weight of the support. In some examples, the outer surfaces consist essentially of stabilized zirconia. In one example, the catalyst consists essentially of platinum on such support. In another example, the catalyst consists essentially of platinum and gold on such support. In other examples, the catalyst further includes palladium. In one example, 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 adipic acid, the process comprising reacting 1,6-hexanediol and oxygen in the presence of a catalyst comprising platinum on a support comprising zirconia or stabilized zirconia thereby producing a reaction mixture comprising adipic acid, wherein the catalyst does not include gold.

2. The process of claim 1, wherein the surface area of the support is equal to or less than about 220 m^2/g.

3. The process of claim 2, wherein the surface area of the support is equal to or less than about 100 m^2/g.

4. The process of claim 2, wherein the average pore diameter of the support is in the range of at least about 5 nanometer to about 70 nanometer.

5. The process of claim 4, wherein the average pore diameter of the support is at least about 10 nm.

6. The process of claim 1, wherein the support further comprises tungsten.

7. The process of claim 6,wherein the tungsten is present in an amount ranging from about 1 wt% to about 15 wt% of the total weight of the support.

8. The process of claim 1, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature in the range of from about 100˚C to about 180˚C.

9. The process of claim 8, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature in the range of from about 135˚C to about 165˚C.

10. The process of claim 1, wherein the reaction is conducted under a partial pressure of oxygen in the range of from about 50 psig to about 2000 psig.

11. The process of claim 10, wherein the reaction is conducted under a partial pressure of oxygen in the range of from about 50 psig to about 1000 psig.

12. The process of claim 11, wherein the reaction is conducted under a partial pressure of oxygen in the range of from about 50 psig to about 750 psig.

13. The process of claim 1, wherein the reaction is conducted in the presence of a solvent.

14. The process of claim 13, wherein the solvent comprises a solvent selected from the group consisting of water, alcohols, esters, ethers, ketones, and mixtures thereof.

15. The process of claim 14, wherein the solvent is water.

16. The process of claim 1, wherein the adipic acid is produced at a yield of at least about 60%.

17. The process of claim 16, wherein the adipic acid is produced at a yield of at least about 70%.

18. The process of claim 17, wherein the adipic acid is produced at a yield of at least about 80%.

19. The process of claim 18, wherein the adipic acid is produced at a yield of at least about 90%.

20. The process of claim 1, further comprising recovering the adipic acid from the reaction mixture.

21. The process of claim 2, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature in the range of from about 100˚C to about 180˚C.

22. The process of claim 12, wherein the reacting the 1,6-hexanediol with oxygen in the presence of a heterogeneous catalyst is carried out at a temperature in the range of from about 100˚C to about 180˚C.