

methods have also been employed; see, for example, U.S. Patent Nos. 6,049,004, 5,599,977, and 6,498,269, WO 2008/021054 and *J. Chem. Technol. Biotechnol.* Vol. 76, p. 186-190 (2001); *J. Agr. Food Chem.* Vol. 1, p.779-783 (1953); *J. Carbohydrate Chem.* Vol. 21, p. 65-77 (2002); *Carbohydrate Res.* Vol. 337, p. 1059-1063 (2002); *Carbohydrate Res.* 336, p. 75-78 (2001); and *Carbohydrate Res.* Vol. 330, p. 21-29 (2001). However, these processes suffer from economic shortcomings resulting from, among other matters, process yield limitations, low conversion rates, and limited selectivity due to shortcomings in the performance of existing catalysts. None of these catalysts or the processes employing them are used industrially for the selective oxidation of glucose-containing carbohydrates to manufacture specialty or industrial carboxylic acids or derivatives thereof.

[0008] Thus, there remains a need for new, industrially scalable catalysts for the selective and commercially-meaningful conversion of a primary hydroxyl group to a carboxyl group of compositions comprising a primary hydroxyl group and at least a secondary hydroxyl group. Desirably, there is the need to convert biorenewable materials such as, for example, carbohydrates or polyols, to specialty or industrial carboxylic acids and derivatives thereof, and more particularly, e.g., to convert glucose (derived from starch, cellulose or sucrose) to important chemicals such as glucaric acid and derivatives thereof.

SUMMARY OF THE INVENTION

[0008a] In a first aspect, the present invention refers to a catalyst composition comprising gold in the form of a gold-containing alloy and particles of platinum on a support wherein (a) the molar ratio of platinum to gold on the support is from about 100:1 to about 1:4 and (b) the particle sizes of the platinum particles are substantially in the range of from about 2 to about 50 nanometers.

[0008b] In a second aspect, the present invention refers to a catalyst composition useful for the selective conversion of a primary alcohol group to a carboxyl group in compositions comprising a primary alcohol group and at least a secondary alcohol wherein the catalyst composition comprises platinum and gold.

[0008c] In a third aspect, the present invention refers to a process for manufacturing an oxidation catalyst comprising the steps of a) providing a support, b) contacting the support with at least one gold-containing compound, c) contacting the support and the at least one gold-containing compound with a base, d) contacting the support with at least one platinum-containing compound, e) treating the support and the at least one platinum-containing compound under conditions sufficient to create on the support particles comprising gold in the form of a gold-containing alloy and particles of platinum, wherein the molar ratio of platinum to gold on the support is from about 100:1 to about 1:4, and the particle sizes of the platinum particles are substantially in the range of from about 2 to about 50 nanometer.

[0008d] In a fourth aspect, the present invention refers to a catalyst composition comprising gold in the form of a gold-containing alloy and particles of platinum on a support wherein the molar ratio of platinum to gold on the support is in the range of from about 100:1 to about 1:4.

[0008e] In a fifth aspect, the present invention refers to a process for preparing glucaric acid or derivatives thereof comprising reacting glucose with a source of oxygen in the presence of the catalyst composition of the present invention and in the substantial absence of added base.

[0009] Furthermore, ~~the present invention~~disclosure is directed generally to catalyst compositions comprising gold and discrete particles of platinum on a support wherein the ratio of platinum to gold on the support is in the range of from about 100:1 to about 1:4 and the platinum is substantially present on the support as Pt(0).

[0010] The present ~~invention~~disclosure is also directed to catalyst compositions useful for the selective conversion of a primary hydroxyl group of compositions comprising a primary hydroxyl group and at least a secondary hydroxyl group to a carboxyl group wherein the catalyst compositions comprise platinum and gold.

[0011] The present ~~invention~~disclosure is further directed to catalyst compositions comprising gold and discrete particles of platinum on a support wherein (a) the ratio of platinum to gold on the support is in the range of from about 100:1 to about 1:4, (b) the platinum is substantially present on the support as Pt(0), and (c) the particle sizes of the platinum particles are substantially in the range of from about 2 to about 50 nanometers.

[0012] Moreover, the present ~~invention~~disclosure is directed to catalyst compositions comprising particles comprising gold and particles of platinum on a support wherein (a) the ratio of platinum to gold on the support is in the range of from about 100:1 to about 1:4, (b) the platinum is substantially present on the support as Pt(0), (c) the particle sizes of the platinum particles are substantially in the range of from about 2 to about 50 nanometers, and (d) the particle sizes of the gold-containing particles are substantially in the range of about 2 to about 20 nanometers.

[0013] Further, the present ~~invention~~disclosure is directed to catalyst compositions produced by processes comprising the steps of a) providing a solid support, b) contacting the support with at least one gold-containing compound, c) contacting the support and the at least one gold-containing compound with a base, d) contacting the support with at least one platinum-containing compound, and e) treating the support and the at least one platinum-containing compound under conditions sufficient to create on the support particles comprising gold and particles comprising platinum, wherein the ratio of platinum to gold on the support is in the range of from about 100:1 to about 1:4, the platinum is substantially present on the support as Pt(0), and the particle sizes of the platinum particles are substantially in the range of from about 2 to about 50 nanometers.

[0014] The present ~~invention~~disclosure is further directed to processes for preparing glucaric acid or derivatives thereof comprising reacting glucose with a source of oxygen in the presence of a catalyst comprising gold and platinum and in the substantial absence of added base.

[0015] Other objects and features will become apparent and/or will be pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 is a TEM photograph of fresh catalyst prepared in accordance with Example 2 (entry 21) comprised of 4 wt% platinum and 4 wt% gold on Saint Gobain Norpro Titania ST31119 particles of 150-250 μm at magnification of 88k.

[0017] Fig. 2 is a TEM photograph of fresh catalyst of the present invention as described with respect to Fig. 1 at magnification of 530k.

[0018] Fig. 3 is a TEM photograph of fresh catalyst of the present invention as described with respect to Fig. 1 at magnification of 530k.

[0019] Fig. 4 is a TEM photograph of fresh catalyst of the present invention as described with respect to Fig. 1 at magnification of 530k.

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WHAT IS CLAIMED IS:

1. A catalyst composition comprising gold in the form of a gold-containing alloy and particles of platinum (0) on a support wherein (a) the molar ratio of platinum to gold on the support is from about 100:1 to about 1:4, and (b) the particle sizes of the platinum (0) particles are substantially in the range of from about 2 to about 50 nanometers.

2. The catalyst composition of claim 1 wherein the support is selected from the group consisting of titanias, zirconias, silicas, zeolites, carbon and montmorillonites.

3. The catalyst composition of claim 1 or 2 wherein the particles sizes of the platinum particles are substantially in the range of from about 5 to about 20 nanometers.

4. The catalyst composition of any of claims 1-3 wherein the particle sizes of the particles comprising gold are substantially in the range of from about 2 to about 20 nanometers.

5. The catalyst composition of any of claims 1-4 wherein at least about 50% of the platinum particles have a size in the range of from about 8 to about 12 nanometers.

6. The catalyst composition of any of claims 1-5 wherein at least about 50% of the gold particles have a size in the range of from about 5 to about 12 nanometers.

7. The catalyst composition of any of claims 1-6 wherein the support is selected from the group consisting of titanias, zirconias and silicas.

8. The catalyst composition of any of claims 1-7 wherein the support comprises titania.

9. The catalyst composition of any of the preceding claims wherein the molar ratio of platinum to gold is in the range of from about 10:1 to about 1:2.

10. The catalyst composition of any of the preceding claims wherein the molar ratio of platinum to gold is in the range of from about 3:1 to about 1:2.

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11. The catalyst composition of any of the preceding claims wherein the molar ratio of platinum to gold is in the range of from about 2:1 to about 1:2.

12. The catalyst composition of any of the preceding claims wherein the total metal loading of the catalyst is about 10 wt% or less.

13. The catalyst composition of any of the preceding claims wherein the total metal loading of the catalyst is from about 1 to about 8 wt%.

14. The catalyst composition of any of the preceding claims wherein the total metal loading of the catalyst is from about 2 to about 4 wt%.

15. A catalyst composition useful for the selective conversion of a primary alcohol group to a carboxyl group in compositions comprising a primary alcohol group and at least a secondary alcohol wherein the catalyst composition comprises platinum and gold.

16. A process for manufacturing an oxidation catalyst comprising the steps of a) providing a support, b) contacting the support with at least one gold-containing compound, c) contacting the support and the at least one gold-containing compound with a base, d) contacting the support with at least one platinum-containing compound, e) treating the support and the at least one platinum-containing compound under conditions sufficient to create on the support particles comprising gold in the form of a gold-containing alloy and particles of platinum (0), wherein the molar ratio of platinum to gold on the support is from about 100:1 to about 1:4, and the particle sizes of the platinum (0) particles are substantially in the range of from about 2 to about 50 nanometer.

17. The process of claim 16 wherein steps b) and c) are undertaken before step d).

18. The process of claim 16 wherein step d) is undertaken prior to step c).

19. The process of claim 17 wherein after the base is added, the support, gold-containing compound and the base are heated.

20. The process of claim 18 wherein the platinum-containing compound is heated prior to contacting the support with the gold-containing compound.

21. The process of claim 16 wherein the treating step comprises heating.

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22. The process of claim 21 wherein the heating is conducted under an oxidizing or reducing environment.

23. The process of claim 21 or 22 wherein the heating is at a temperature of about 500°C or less.

24. A catalyst composition comprising gold in the form of a gold-containing alloy and particles of platinum (0) on a support wherein the molar ratio of platinum to gold on the support is in the range of from about 100:1 to about 1:4.

25. A process for preparing glucaric acid or derivatives thereof comprising reacting glucose with a source of oxygen in the presence of a catalyst comprising gold and platinum and in the substantial absence of added base.

26. The catalyst composition of claim 1 comprising gold in the form of a platinum-gold alloy.

WHAT IS CLAIMED IS:

1. A catalyst composition comprising gold in the form of a gold-containing alloy and particles of platinum (0) on a support wherein (a) the molar ratio of platinum to gold on the support is from about 100:1 to about 1:4 and (b) the particle sizes of the platinum (0) particles are substantially in the range of from about 2 to about 50 nanometers.
2. The catalyst composition of claim 1 wherein the support is selected from the group consisting of titanias, zirconias, silicas, zeolites, carbon and montmorillonites.
3. The catalyst composition of claim 1 or 2 wherein the particles sizes of the platinum particles are substantially in the range of from about 5 to about 20 nanometers.
4. The catalyst composition of any of claims 1-3 wherein the particle sizes of the particles comprising gold are substantially in the range of from about 2 to about 20 nanometers.
5. The catalyst composition of any of claims 1-4 wherein at least about 50% of the platinum particles have a size in the range of from about 8 to about 12 nanometers.
6. The catalyst composition of any of claims 1-5 wherein at least about 50% of the gold particles have a size in the range of from about 5 to about 12 nanometers.
7. The catalyst composition of any of claims 1-6 wherein the support is selected from the group consisting of titanias, zirconias and silicas.
8. The catalyst composition of any of claims 1-7 wherein the support comprises titania.
9. The catalyst composition of any of the preceding claims wherein the molar ratio of platinum to gold is in the range of from about 10:1 to about 1:2.
10. The catalyst composition of any of the preceding claims wherein the molar ratio of platinum to gold is in the range of from about 3:1 to about 1:2.
11. The catalyst composition of any of the preceding claims wherein the molar ratio of platinum to gold is in the range of from about 2:1 to about 1:2.
12. The catalyst composition of any of the preceding claims wherein the total metal loading of the catalyst is about 10 wt% or less.

13. The catalyst composition of any of the preceding claims wherein the total metal loading of the catalyst is from about 1 to about 8 wt%.

14. The catalyst composition of any of the preceding claims wherein the total metal loading of the catalyst is from about 2 to about 4 wt%.

15. A catalyst composition useful for the selective conversion of a primary alcohol group to a carboxyl group in compositions comprising a primary alcohol group and at least a secondary alcohol wherein the catalyst composition comprises platinum and gold.

16. A process for manufacturing an oxidation catalyst comprising the steps of a) providing a support, b) contacting the support with at least one gold-containing compound, c) contacting the support and the at least one gold-containing compound with a base, d) contacting the support with at least one platinum-containing compound, e) treating the support and the at least one platinum-containing compound under conditions sufficient to create on the support particles comprising gold in the form of a gold-containing alloy and particles of platinum (0), wherein the molar ratio of platinum to gold on the support is from about 100:1 to about 1:4, and the particle sizes of the platinum (0) particles are substantially in the range of from about 2 to about 50 nanometer.

17. The process of claim 16 wherein steps b) and c) are undertaken before step d).

18. The process of claim 16 wherein step d) is undertaken prior to step c).

19. The process of claim 17 wherein after the base is added, the support, gold-containing compound and the base are heated.

20. The process of claim 18 wherein the platinum-containing compound is heated prior to contacting the support with the gold-containing compound.

21. The process of claim 16 wherein the treating step comprises heating.

22. The process of claim 21 wherein the heating is conducted under an oxidizing or reducing environment.

23. The process of claim 21 or 22 wherein the heating is at a temperature of about 500°C or less.

24. A catalyst composition comprising gold in the form of a gold-containing alloy and particles of platinum (0) on a support wherein the molar ratio of platinum to gold on the support is in the range of from about 100:1 to about 1:4.

25. A process for preparing glucaric acid or derivatives thereof comprising reacting glucose with a source of oxygen in the presence of the catalyst composition of any one of claims 1-15 and 26 and in the substantial absence of added base.

26. The catalyst composition of claim 1 comprising gold in the form of a platinum-gold alloy.