clearly demonstrate the need for development of alternative, more efficient processes for the production of HDO.

SUMMARY

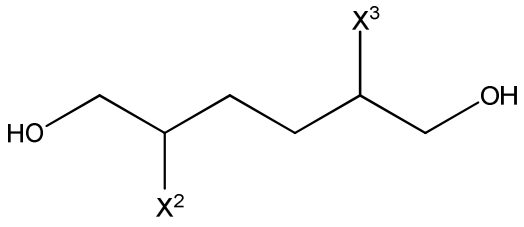
[0011] Briefly, therefore, the present disclosure is directed to processes for preparing hexamethylenediamine from a carbohydrate source by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst to produce 1,6-hexanediol; and, converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. The present disclosure is also directed to processes for preparing hexamethylenediamine from a carbohydrate source by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce a reaction product comprising 1,2,6-hexanetriol; converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol; and converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. In some examples, the heterogeneous reduction catalyst comprises Pt. In other examples, the heterogeneous reduction catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re. In other examples, the step of converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol is conducted in the presence of hydrogen and a hydrogenation catalyst comprising Pt. In other examples, the yield of 1,6-hexanediol is at least about 40%. In other examples, the yield of 1,6-hexanediol is at least about 50%. In other examples, the yield of 1,6-hexanediol is at least about 60%. In other examples, the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other examples, the furfural substrate is 5-hydroxymethylfurfural. In other examples, the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose. In other examples, the catalyst further comprises a support selected from the group consisting of zirconias, silicas and zeolites. In other examples, the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 100°C and about 180°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other examples, the hydrogenation catalyst comprises Pt and W supported on zirconia. The present disclosure is also directed to hexamethylenediamine produced by the processes of any of the above examples.

[0012] The present disclosure is also directed to processes for preparing 1,6-hexanediol from a carbohydrate source by converting the carbohydrate source to a furfural substrate; and, reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol. The present disclosure is also directed to processes for preparing 1,6-hexanediol from a carbohydrate source by converting the carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a Pt containing heterogeneous reduction catalyst to produce a reaction product comprising 1,2,6-hexanetriol; and, converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol. In some examples, the heterogeneous catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re. In other examples, the step of converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol is conducted in the presence of hydrogen and a hydrogenation catalyst comprising Pt. In other examples, the hydrogenation catalyst is a supported heterogeneous catalyst. In other examples, the yield of 1,6-hexanediol from the furfural substrate is at least 40%. In other examples, the yield of 1,6-hexanediol from the furfural substrate is at least 50%. In other examples, the yield of 1,6-hexanediol from the furfural substrate is at least 60%. In other examples, the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other examples, the furfural substrate is 5-hydroxymethylfurfural. In other examples, the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose. In other examples, the catalyst further comprises a support selected from the group consisting of zirconias, silicas and zeolites. In other examples, the reaction of the furfural substrate with hydrogen to produce 1,2,6-hexanetriol is carried out at a temperature in the range of about 100°C and about 140°C and a pressure of hydrogen in the range of about 200 psig to about 1000 psig. In other examples, the catalyst comprises Pt and W supported on zirconia. The present disclosure is also directed to 1,6-hexanediol produced by the processes of any of the above examples.

[0013] The present disclosure is also directed to processes for preparing hexamethylenediamine from a carbohydrate source by: (a) converting a carbohydrate source to a furfural substrate; (b) reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to a reaction product comprising 1,2,6-hexanetriol; (c) reacting at least a portion of the 1,2,6-hexanetriol with

hydrogen in the presence of the heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol; and (d) converting at least a portion of the 1,6-hexanediol to hexamethylenediamine, wherein steps b) and c) are conducted in a single reactor. The present disclosure is also directed to processes for preparing 1,6-hexanediol from a carbohydrate source by: (a) converting a carbohydrate source to a furfural substrate; (b) reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to a reaction product comprising 1,2,6-hexanetriol; and (c) reacting at least a portion of the 1,2,6-hexanetriol with hydrogen in the presence of the heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol, wherein steps b) and c) are conducted in a single reactor. In some examples, the heterogeneous reduction catalyst further comprises W. In other examples, steps (b) and (c) are carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other examples, the Pt containing catalysts of steps b) and c) are different and the temperatures and pressures at which steps b) and c) are conducted are substantially the same. In other examples, the temperatures and pressures at which steps b) and c) are conducted are different. In other examples, step b) is conducted at a temperature in the range of about 100°C to about 140°C and a pressure in the range of about 200 psig to about 1000 psig and step c) is conducted at a temperature in the range of about 120°C to about 180°C and a pressure in the range of about 200 psig to about 2000 psig. In other examples, the yield of 1,6-hexanediol from the furfural substrate is at least about 40%. In other examples, the yield of 1,6-hexanediol from the furfural substrate is at least about 50%. In other examples, the yield of 1,6-hexanediol from the furfural substrate is at least about 60%. In other examples, the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose. In other examples, steps (b) and (c) are carried out in one reaction zone. In other examples, the catalyst comprises Pt and W supported on zirconia. The present disclosure is also directed to hexamethylenediamine produced by the processes of any of the above examples. The present disclosure is also directed to 1,6-hexanediol prepared by the process of any of the above examples.

[0014] The present disclosure is also directed to processes for preparing a compound of formula II



(II);

[0015] wherein each of X^2 and X^3 is selected from the group of hydrogen and hydroxyl; by converting a carbohydrate source to a furfural substrate; and, reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce the compound of formula II. In some examples, the catalyst further comprises W. In other examples, the catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re.

[0015a] In one aspect, there is provided a process for preparing a product comprising 1,2,6-hexanetriol, wherein the process comprises reacting 5-(hydroxymethyl)furfural (HMF) with hydrogen in the presence of a heterogeneous catalyst comprising Pt to produce a product comprising 1,2,6-hexanetriol.

DETAILED DESCRIPTION

[0016] The following description sets forth exemplary methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present invention.

[0017] In accordance with the present invention, applicants disclose processes for the chemocatalytic conversion of a furfural substrate, which may be derived from a carbohydrate source (e.g., glucose or fructose) to hexamethylenediamine, and intermediate processes and products along the pathway. In some embodiments, the processes are carried out by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst to produce 1,6-hexanediol; and, converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. In other embodiments, the processes are carried out by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce a reaction product comprising 1,2,6-hexanetriol; converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol; and converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. In some embodiments, the processes are carried out by converting the carbohydrate source to a furfural substrate; and, reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol. In other embodiments, the processes are carried out by converting

CLAIMS

We claim:

1. A process for preparing a product comprising 1,2,6-hexanetriol, wherein the process comprises reacting 5-(hydroxymethyl)furfural (HMF) with hydrogen in the presence of a heterogeneous catalyst comprising Pt to produce a product comprising 1,2,6-hexanetriol.

2. The process of claim 1, wherein the reaction of the HMF with hydrogen is carried out at a temperature in the range of about 60° C. to about 200° C. and a pressure in the range of from about 200 psig to about 2000 psig.

3. The process of claim 1, wherein the reaction of the HMF with hydrogen is carried out at a temperature in the range of from about 100° C. to about 140° C.

4. The process of claim 1, wherein the heterogeneous catalyst further comprises at least one metal (M2) selected from the group consisting of Mo, La, Sm, Y, W, and Re.

5. The process of claim 4, wherein M2 is W.

6. The process of claim 4, wherein M2 is Mo.

7. The process of claim 4, wherein M2 is La.

8. The process of claim 4, wherein M2 is Sm.

9. The process of claim 4, wherein the molar ratio of Pt to M2 is in the range of from about 20:1 to about 1:10.

10. The process of claim 9, wherein the molar ratio of Pt to M2 is in the range of from about 10:1 to about 1:5.

11. The process of claim 10, wherein the molar ratio of Pt to M2 is in the range of from about 8:1 to about 1:2.

12. The process of claim 1, wherein the heterogeneous catalyst is a supported heterogeneous catalyst.

13. The process of claim 12, wherein the supported heterogeneous catalyst comprises a support selected from the group consisting of acidic ion-exchange resin, gamma alumina, fluorinated alumina, sulfate or tungsten promoted zirconia, titania, silica, silica promoted alumina, aluminum phosphate, tungsten oxide supported on silica-alumina, acidic clay, supported mineral acid and zeolites.

14. The process of claim 12, wherein the supported heterogeneous catalyst comprises a support selected from the group consisting of metal-doped titania, metal-doped zirconia, metal-doped ceria and metal-modified niobia.

15. The process of claim 12, wherein the supported heterogeneous catalyst comprises a support selected from the group consisting of a zirconia, a silica, and a zeolite.

16. The process of claim 4, wherein the heterogeneous catalyst is a supported heterogeneous catalyst.

17. The process of claim 16, wherein the supported heterogeneous catalyst comprises a support selected from the group consisting of acidic ion-exchange resin, gamma alumina, fluorinated alumina, sulfate or tungsten promoted zirconia, titania, silica, silica promoted alumina, aluminum phosphate, tungsten oxide supported on silica-alumina, acidic clay, supported mineral acid and zeolites.

18. The process of claim 16, wherein the supported heterogeneous catalyst comprises a support selected from the group consisting of metal-doped titania, metal-doped zirconia, metal-doped ceria and metal-modified niobia.

19. The process of claim 16, wherein the supported heterogeneous catalyst comprises a support selected from the group consisting of a zirconia, a silica, and a zeolite.

20. The process of claim 16, wherein the heterogeneous catalyst comprises a total weight of metal that is in the range of from about 0.1 % to about 10% of the total weight of the catalyst.

21. The process of claim 16, wherein the heterogeneous catalyst comprises a total weight of metal that is in the range of from about 0.2% to about 8% of the total weight of the catalyst.

22. The process of claim 16, wherein the catalyst com-prises a total weight of metal that is in the range of from about 0.2% to about 5% of the total weight of the catalyst.

23. The process of claim 16, wherein the heterogeneous catalyst comprises a total weight of metal that is less than about 4% of the total weight of the catalyst.

24. The process of claim 1, wherein the process is conducted in the presence of a solvent selected from the group consisting of water, an alcohol, an ester, an ether, a ketone, and a mixture thereof.

25. The process of claim 24, wherein the solvent comprises water.

26. The process of claim 4, wherein the process is conducted in the presence of a solvent selected from the group consisting of water, an alcohol, an ester, an ether, a ketone, and a mixture thereof.

27. The process of claim 26, wherein the solvent comprises water.