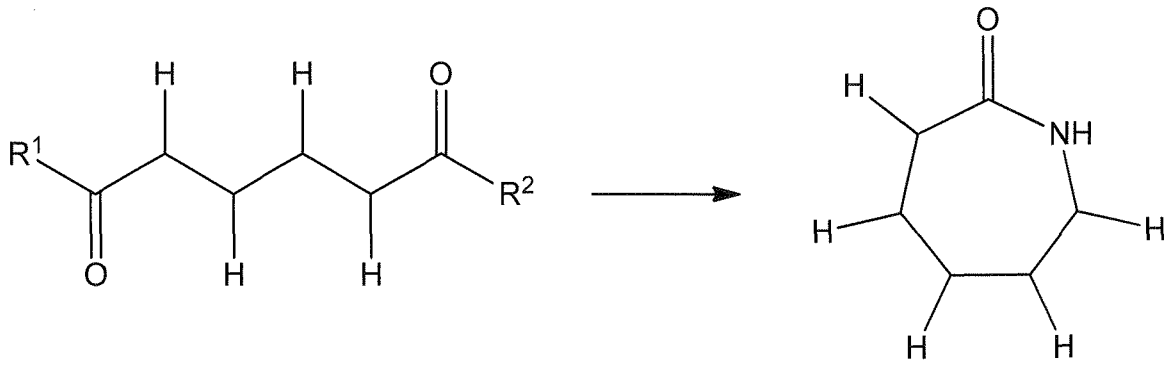
SUMMARY

[0009] Briefly, therefore, the present disclosure is directed to processes for preparing caprolactam from an adipic acid substrate obtained from biorenewable materials. Generally, the process for preparing caprolactam from an adipic acid substrate comprises converting at least a portion of the adipic acid substrate to caprolactam in the presence of ammonia and hydrogen and particular heterogeneous catalysts and, preferably, particular solvents. ~~In one aspect, there is disclosed herein a process for preparing a caprolactam product, the process comprising chemocatalytically converting an adipic acid substrate to a caprolactam product, wherein the step of chemocatalytically converting the adipic acid substrate to the caprolactam product comprises reacting the adipic acid substrate with hydrogen and ammonia in the presence of a heterogeneous catalyst and a solvent comprising tert-butanol.~~ In ~~another~~ one aspect, there is disclosed a process for preparing a caprolactam product, the process comprising: reacting an adipic acid substrate, hydrogen, and ammonia, in the presence of a heterogeneous catalyst comprising at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof, on a support that is, in the absence of the at least one metal, capable of catalyzing the reaction of the adipic acid substrate and ammonia to produce an amide, and solvent, to convert at least a portion of the adipic acid substrate to the caprolactam product, wherein the adipic acid substrate is a compound of formula I, and wherein the caprolactam product is a compound of formula II

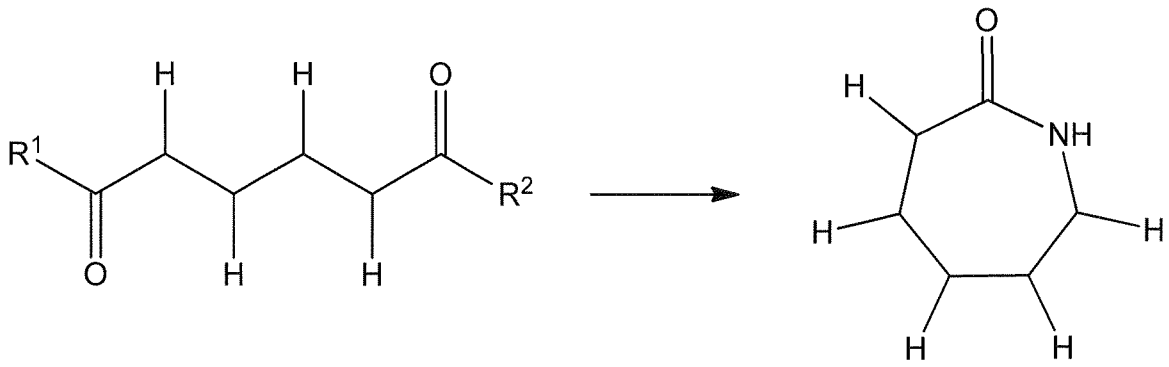


(I) (II)

wherein each R^1 and R^2 is independently OR^a and NH_2; wherein each R^a is independently selected from the group consisting of hydrogen, alkyl, and a salt-forming ion; and wherein the support of the heterogeneous catalyst comprises a material selected from the group consisting of titanias, zirconias, and mixtures thereof. In yet another aspect, there is disclosed a process for producing nylon 6, the process comprising: preparing a caprolactam product in accordance with the process as described herein, and converting at least a portion of the caprolactam product into nylon 6. ~~In a further aspect, there is disclosed a process for producing caprolactam from adipic acid, the process comprising the steps of a) converting at least a portion of the adipic acid to at least one amide selected from the group of 6-amino-6-~~

~~oxohexanoic acid and adipamide in the presence of a metal oxide comprising titania, zirconia, or a mixture thereof, b) reducing the at least one amide to at least one of aminocaproic acid and aminocaproamide, and c) cyclizing at least a portion of the aminocaproic acid and/or aminocaproamide produced from b), above, to caprolactam, wherein at least one of b) and c), above, is carried out in the presence of at least one metal selected from the group of Ru, Pt, Pd, Rh, Ir, and Os. In one aspect, there is disclosed a catalyst comprising ruthenium and rhenium on a support comprising titania, wherein the catalyst is capable of catalyzing the conversion of adipic acid to caprolactam.~~

[0010] The present disclosure is directed to processes for preparing a caprolactam product by chemocatalytically converting an adipic acid substrate to a caprolactam product, wherein the step of chemocatalytically converting the adipic acid substrate to the caprolactam product comprises reacting the adipic acid substrate with hydrogen and ammonia in the presence of a heterogeneous catalyst and a solvent comprising tert-butanol. The present disclosure is also directed to processes for preparing a caprolactam product by reacting an adipic acid substrate, hydrogen and ammonia, in the presence of a heterogeneous catalyst comprising at least one metal selected from the group of Ru, Rh, Pd, Pt, Ir, and Os, and mixtures thereof, on a support that is, in the absence of the at least one metal, capable of catalyzing the reaction of the adipic acid substrate and ammonia to produce an amide, and solvent, to convert at least a portion of the adipic acid substrate to the caprolactam product, wherein the adipic acid substrate is a compound of formula I, and wherein the caprolactam product is a compound of formula II



(I) (II)

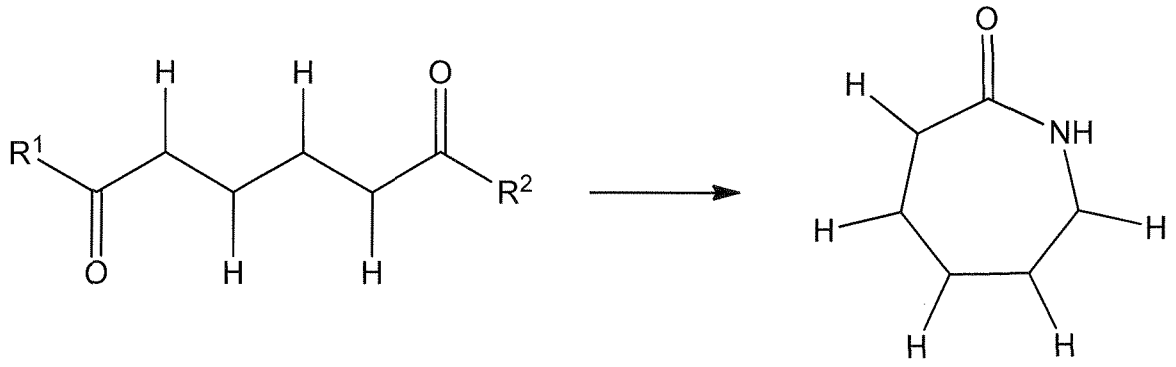
wherein each R^1 and R^2 is independently hydroxyl, OR^a and NH_2; and wherein each R^a is independently selected from the group consisting of hydrogen, alkyl, and a salt-forming ion. In some examples, reacting the adipic acid substrate with hydrogen and ammonia in the

CLAIMS

WE CLAIM:

1. A process for preparing a caprolactam product, the process comprising:

reacting an adipic acid substrate, hydrogen, and ammonia, in the presence of a heterogeneous catalyst comprising at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof, on a support that is, in the absence of the at least one metal, capable of catalyzing the reaction of the adipic acid substrate and ammonia to produce an amide, and solvent, to convert at least a portion of the adipic acid substrate to the caprolactam product, wherein the adipic acid substrate is a compound of formula I, and wherein the caprolactam product is a compound of formula II



(I) (II)

wherein each R^1 and R^2 is independently OR^a and NH_2;

wherein each R^a is independently selected from the group consisting of hydrogen, alkyl, and a salt-forming ion; and wherein the support of the heterogeneous catalyst comprises a material selected from the group consisting of titanias, zirconias, and mixtures thereof.

2. The process of claim 1, wherein the metal weight of the at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof is from about 0.2 wt.% to about 10% of the total weight of the catalyst.

3. The process of claim 1, wherein the metal weight of the at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof is from about 0.2 wt.% to about 5% of the total weight of the catalyst.

4. The process of claim 1, wherein the adipic acid substrate comprises adipic acid; the heterogeneous catalyst comprises ruthenium; the weight of ruthenium is from about 0.2 wt.% to about 5% of the total weight of the catalyst; and the reaction is conducted at a temperature from about 20°C to about 200°C.

5. The process of claim 1, wherein the reaction is conducted at a temperature in the range of from about 20°C to about 200°C.

6. The process of any of claims 1-5, wherein the adipic acid substrate is derived from a carbohydrate source.

7. The process of any of claims 1-6, wherein the adipic acid substrate comprises adipic acid.

8. The process of any of claims 1-7, wherein the heterogeneous catalyst comprises ruthenium.

9. The process of claim any of claims 1-8, wherein the heterogeneous catalyst comprises Ru and further comprises a second metal selected from the group consisting of Fe, Co, Ni, Cu, W, and Re.

10. The process of any of claims 1-9, wherein the support comprises titania.

11. The process of any of claims 1-10, wherein the solvent is selected from the group of water, alcohols which do not react with the adipic acid substrate, ethers, and mixtures thereof.

12. The process of any of claims 1-11, wherein the solvent is selected from the group consisting of tert-butanol, tert-butanol – water mixtures, and tert-butanol – ammonia mixtures.

13. The process of any of claims 1-12, wherein the solvent comprises up to about 30% by volume water.

14. The process of any of claims 1-12, wherein the solvent comprises up to about 30% by volume of water and wherein the volume of solvent is equal to or less than about 80% of the total volume of liquid.

15. The process of claim 9, wherein the molar ratio of Ru to second metal is in the range of from about 100:1 to about 1:10.

16. The process of any of claims 1-12, 14, and 15, wherein the solvent comprises up to about 30% by volume of a solution of ammonia and water.

17. The process of any of claims 1-12, 14, and 15, wherein the ammonia is a solution or a gas.

18. The process of any of claims 1-17, wherein the reaction is conducted under a partial pressure of hydrogen in the range of from about 200 psi to about 2000 psi.

19. The process of any of claims 1-18, wherein caprolactam is produced in at least about 50% yield from the adipic acid substrate.

20. The process of any of claims 1-19, wherein the reaction is carried out as a continuous process.

21. The process of any of claims 1-20, wherein the reaction is carried out in at least one fixed bed reactor.

22. The process of any of claims 1-21, wherein the heterogeneous catalyst comprises ruthenium and rhenium and the support comprises titania.

23. The process of claim 22, wherein the metal weight of ruthenium and rhenium is from about 0.2 wt.% to about 5% of the total weight of the catalyst and the ratio of ruthenium to rhenium is from about 10:1 to about 1:5.

24. The process of claim 22 or 23, wherein at least a portion of the titania is in the anatase phase.

25. A process for producing nylon 6, the process comprising:

preparing a caprolactam product in accordance with the process of any of claims 1-24, and converting at least a portion of the caprolactam product into nylon 6.

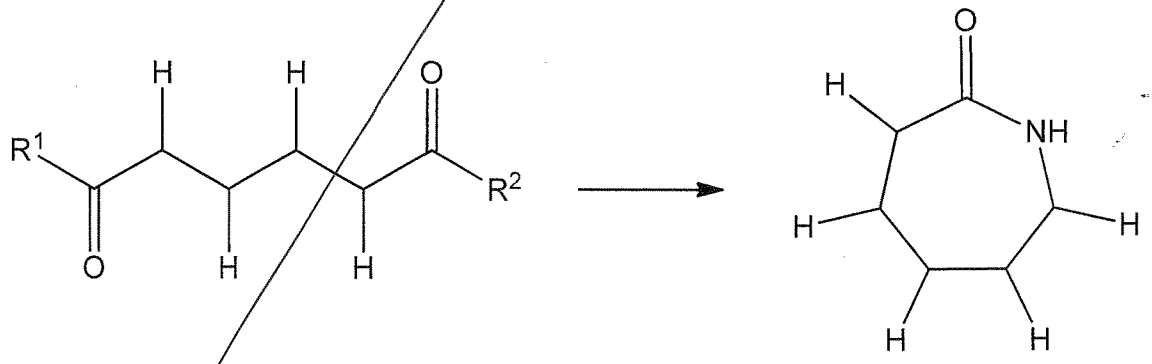
CLAIMS

We claim:

1. A process for preparing a caprolactam product, the process comprising chemocatalytically converting an adipic acid substrate to a caprolactam product, wherein the step of chemocatalytically converting the adipic acid substrate to the caprolactam product comprises reacting the adipic acid substrate with hydrogen and ammonia in the presence of a heterogeneous catalyst and a solvent comprising tert-butanol.

2. A process for preparing a caprolactam product, the process comprising:

reacting an adipic acid substrate, hydrogen, and ammonia, in the presence of a heterogeneous catalyst comprising at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof, on a support that is, in the absence of the at least one metal, capable of catalyzing the reaction of the adipic acid substrate and ammonia to produce an amide, and solvent, to convert at least a portion of the adipic acid substrate to the caprolactam product, wherein the adipic acid substrate is a compound of formula I, and wherein the caprolactam product is a compound of formula II



(I) (II)

wherein each R^1 and R^2 is independently OR^a and NH_2;

wherein each R^a is independently selected from the group consisting of hydrogen, alkyl, and a salt-forming ion.

3. The process of claim 1, wherein the heterogeneous catalyst comprises at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof, on a support.

4. The process of claim 2 or 3, wherein the metal weight of the at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof is from about 0.2 wt.% to about 10% of the total weight of the catalyst.

5. The process of claim 2 or 3, wherein the metal weight of the at least one metal selected from the group of Ru, Rh, Pt, Pd, Ir, and Os, and mixtures thereof is from about 0.2 wt.% to about 5% of the total weight of the catalyst.

6. The process of claim 2 or 3, wherein the adipic acid substrate comprises adipic acid; the heterogeneous catalyst comprises ruthenium; the weight of ruthenium is from about 0.2 wt.% to about 5% of the total weight of the catalyst; the support of the heterogeneous catalyst comprises a material selected from the group consisting of titanias, zirconias, and mixtures thereof; and the reaction is conducted at a temperature from about 20°C to about 200°C.

7. The process of claim 1 or 2, wherein the reaction is conducted at a temperature in the range of from about 20°C to about 200°C.

8. The process of claim 3, wherein the support of the heterogeneous catalyst comprises a material selected from the group consisting of titanias, zirconias, and mixtures thereof.

9. The process of claim 3, wherein the support of the heterogeneous catalyst comprises titania.

10. The process of any one of claims 1-9, the adipic acid substrate is derived from a carbohydrate source.

11. The process of any one of claims 1 -10, wherein the adipic acid substrate comprises adipic acid.

12. The process of claim 1 or 2, wherein the heterogeneous catalyst comprises ruthenium.

13. The process of claim 2 or 3, wherein the heterogeneous catalyst comprises Ru and further comprises a second metal selected from the group consisting of Fe, Co, Ni, Cu, W, and Re.

14. The process of claim 2 or 3, wherein the support of the heterogeneous catalyst comprises a material selected from the group consisting of titanias, zirconias, and mixtures thereof.

15. The process of claim 14, wherein the support comprises titania.

16. The process of claim 2-15 wherein the solvent is selected from the group of water, alcohols which do not react with the adipic acid substrate, ethers, and mixtures thereof.

17. The process of claim 16, wherein the solvent is selected from the group consisting of tert-butanol, tert-butanol – water mixtures, and tert-butanol – ammonia mixtures.

18. The process of any of claims 1-17, wherein the solvent comprises up to about 30% by volume water.

19. The process of any of claims 3-9 wherein the solvent comprises up to about 30% by volume of water and wherein the volume of solvent is equal to or less than about 80% of the total volume of liquid .

20. The process of claim 13, wherein the molar ratio of Ru to second metal is in the range of from about 100:1 to about 1:10.

21. The process of any of claims 1-17 and 19, wherein the solvent comprises up to about 30% by volume of a solution of ammonia and water.

22. The process of any one of claims 1-16 and 18-20, wherein the ammonia is a solution or a gas.

23. The process of any one of claims 1-22, wherein the reaction is conducted under a partial pressure of hydrogen in the range of from about 200 psi to about 2000 psi.

24. The process of claim 2, wherein caprolactam is produced in at least about 50% yield from the adipic acid substrate.

25. The process of any one of claims 1-24, wherein the reaction is carried out as a continuous process.

26. The process of any one of claims 1-25, wherein the reaction is carried out in at least one fixed bed reactor.

27. A process for producing nylon 6, the process comprising:

preparing a caprolactam product in accordance with the process of any one of claims 1 to 26, and

converting at least a portion of the caprolactam product into nylon 6.

28. Caprolactam produced by the process of any one of claims 1-26.

29. A process for producing caprolactam from adipic acid, the process comprising the steps of:

a) converting at least a portion of the adipic acid to at least one amide selected from the group of 6-amino-6-oxohexanoic acid and adipamide in the presence of a metal oxide comprising titania, zirconia, or a mixture thereof,

b) reducing the at least one amide to at least one of aminocaproic acid and aminocaproamide, and

c) cyclizing at least a portion of the aminocaproic acid and/or aminocaproamide produced from b), above, to caprolactam, wherein at least one of b) and c), above, is carried out in the presence of at least one metal selected from the group of Ru, Pt, Pd, Rh, Ir, and Os.

30. The process of claim 29 wherein the at least one metal is Ru.

31. The process of claim 30 wherein Re is also present when carrying out at least one of b) and c).

32. The process of claim 30 or 31 wherein a solvent comprising tert-butanol is present in at least one of a), b), and c).

33. The process of any of claims 29 to 32 wherein c) is conducted in the presence of at least one of titania or zirconia, or mixtures thereof.

34. A catalyst comprising ruthenium and rhenium on a support comprising titania, wherein the catalyst is capable of catalyzing the conversion of adipic acid to caprolactam.

35. The catalyst of claim 34 wherein the metal weight of ruthenium and rhenium is from about 0.2 wt.% to about 5% of the total weight of the catalyst and the ratio of ruthenium to rhenium is from about 10:1 to about 1:5.

36. The catalyst of claim 35 wherein at least a portion of the titania is in the anatase phase.