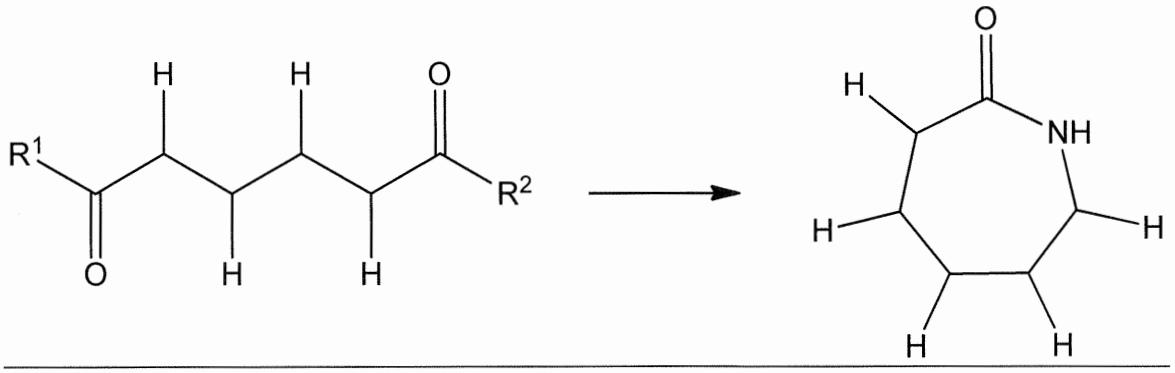
SUMMARY

[0009] Briefly, therefore, the present ~~invention~~ 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 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

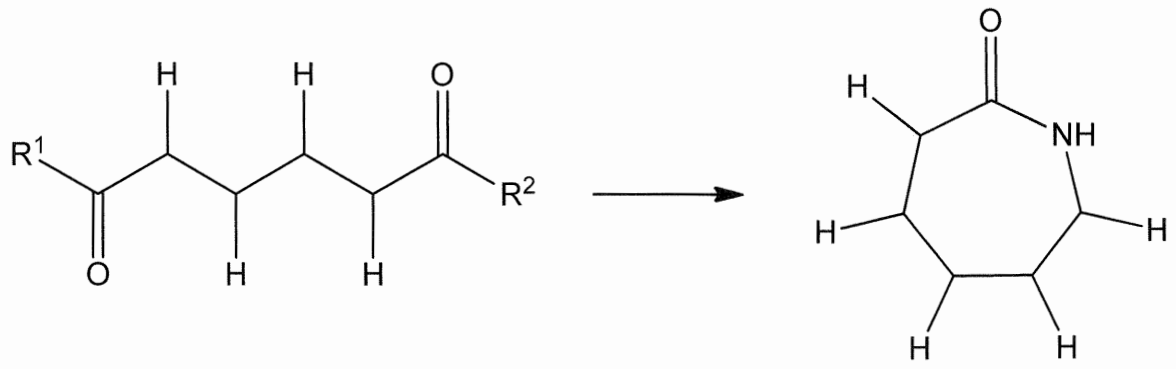


(I) (II)

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. 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 ~~invention~~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 ~~invention~~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 ~~embodiments~~examples, reacting the adipic acid substrate with hydrogen and ammonia in the

presence of the heterogeneous catalyst and solvent comprises: a) combining the adipic acid substrate, the ammonia, the heterogeneous catalyst, and solvent; and b) contacting the combined adipic acid substrate, ammonia, heterogeneous catalyst, and solvent with hydrogen. In some ~~embodiments~~examples, reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises: a) combining the adipic acid substrate, ammonia, and solvent; and b) contacting the combined adipic acid substrate, ammonia, and solvent with a heterogeneous catalyst and hydrogen. In some ~~embodiments~~examples, reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and a solvent comprises: a) combining the adipic acid substrate, ammonia, solvent, and heterogeneous catalyst at a temperature between room temperature and about 200°C; and b) contacting with hydrogen the combined adipic acid substrate, ammonia, solvent, and heterogeneous catalyst. In some ~~embodiments~~examples, reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises: a) contacting the heterogeneous catalyst with hydrogen; b) adding the adipic acid substrate, the ammonia, and the solvent to the heterogeneous catalyst contacted with hydrogen. In some ~~embodiments~~examples, reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises: a) contacting the heterogeneous catalyst with solvent at a temperature in the range of from about room temperature to about 200°C; and b) contacting the heterogeneous catalyst and solvent with the adipic acid substrate, ammonia, and hydrogen. In some ~~embodiments~~examples, reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises: a) contacting the adipic acid substrate with water; and b) contacting the adipic acid substrate and water with solvent, ammonia, hydrogen, and catalyst. In some ~~embodiments~~examples, reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises: a) combining the adipic acid substrate with water and ammonia; and b) contacting the combination with hydrogen, solvent, and the catalyst. In some ~~embodiments~~examples, the adipic acid substrate is derived from a carbohydrate source. In some ~~embodiments~~examples, the adipic acid substrate is selected from the group consisting of adipic acid, a mono-ester of adipic acid, a di-ester of adipic acid, a mono-amide of adipic acid, and a di-amide of adipic acid, or salts thereof. In some ~~embodiments~~examples, the heterogeneous catalyst comprises ruthenium. In some ~~embodiments~~examples, the heterogeneous catalyst comprises a first metal and a second metal, wherein the first metal is Ru and the second metal is selected from the group consisting of Fe, Co, Ni, Cu, W, and Re. In some ~~embodiments~~examples, the support of the heterogeneous catalyst comprises a material selected from the group consisting of

titanias, zirconias, and mixtures thereof. In some ~~embodiments~~examples, the support comprises titania. In some ~~embodiments~~examples, the solvent is selected from the group of water, alcohols which do not react with the adipic acid substrate, ethers, and mixtures thereof. In some ~~embodiments~~examples, the solvent is selected from the group consisting of tert-butanol, tert-butanol – water mixtures, and tert-butanol – ammonia mixtures. In some ~~embodiments~~examples, the solvent comprises up to about 30% by volume water. In some ~~embodiments~~examples, the solvent comprises up to about 30% by volume of water and the volume of solvent is equal to or less than about 80% of the total volume of liquid in the reaction. In some ~~embodiments~~examples, the molar ratio of first metal to second metal is in the range of from about 100:1 to about 1:10. In some ~~embodiments~~examples, the solvent comprises up to about 30% by volume of a solution of ammonia and water. In some ~~embodiments~~examples, the ammonia is a solution or a gas. In some ~~embodiments~~examples, the reaction is conducted under a partial pressure of hydrogen in the range of from about 200 psi to about 2000 psi. In some ~~embodiments~~examples, caprolactam is produced in at least about 50% yield from the adipic acid substrate. In some ~~embodiments~~examples, the reaction is carried out as a continuous process. In some ~~embodiments~~examples, the reaction is carried out in at least one fixed bed reactor. The present ~~invention~~disclosure is also directed to a process for producing nylon 6 by converting caprolactam produced at least in part by any of the above processes and/or ~~embodiments~~examples. The present ~~invention~~disclosure is also directed to caprolactam produced by any of the above processes and/or ~~embodiments~~examples.

[0011] The present ~~invention~~disclosure is also directed to a process for producing caprolactam from adipic acid by 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 some ~~embodiments~~examples, the at least one metal is Ru. In some ~~embodiments~~examples, Re is also present when carrying out at least one of b) and c). In some ~~embodiments~~examples, a solvent comprising tert-butanol is present in at least one of a), b), and c). In some ~~embodiments~~examples, c) is conducted in the presence of at least one of titania or zirconia, or mixtures thereof.

[0012] The present ~~invention~~disclosure is also directed to a catalyst useful for the production of caprolactam comprising ruthenium and rhenium on a support comprising at least one of titania or zirconia. In some ~~embodiments~~examples, the support comprises titania. In other ~~embodiments~~examples, at least a portion of the titania is in the anatase phase.

DETAILED DESCRIPTION

[0013] The following description sets forth exemplary processes, 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.

[0014] Disclosed herein are processes for the chemocatalytic conversion of adipic acid and derivatives thereof to caprolactam. Generally, the processes for producing caprolactam comprises converting adipic acid and derivatives thereof by processes which employ ammonia, hydrogen, suitable catalysts and, preferably, particular solvents. Adipic acid derivatives used as a substrate in the processes described herein may include, for example, mono-esters of adipic acid, di-esters of adipic acid, mono-amides of adipic acid, di-amides of adipic acid, and salts and mixtures thereof.

[0015] The caprolactam prepared in accordance with the disclosed processes may be converted to various other industrially significant chemicals (*e.g.*, nylon 6) according to processes known in the art.

I. Feedstocks

[0016] Adipic acid may be obtained from various carbohydrate-containing sources including conventional biorenewable sources such as corn grain (maize), sugar cane, sugar beet, wheat, potato, cassava and rice as well as alternative sources such as energy crops, plant biomass, agricultural wastes, forestry residues, sugar processing residues and plant-derived household wastes. More generally, biorenewable sources that may be used in accordance with the present invention include any renewable organic matter that includes a source of carbohydrates such as, for example, switch grass, miscanthus, trees (hardwood and softwood), vegetation, and crop residues (e.g., bagasse and corn stover). Other sources may include, for example, waste materials (e.g., spent paper, green waste, municipal waste, etc.).

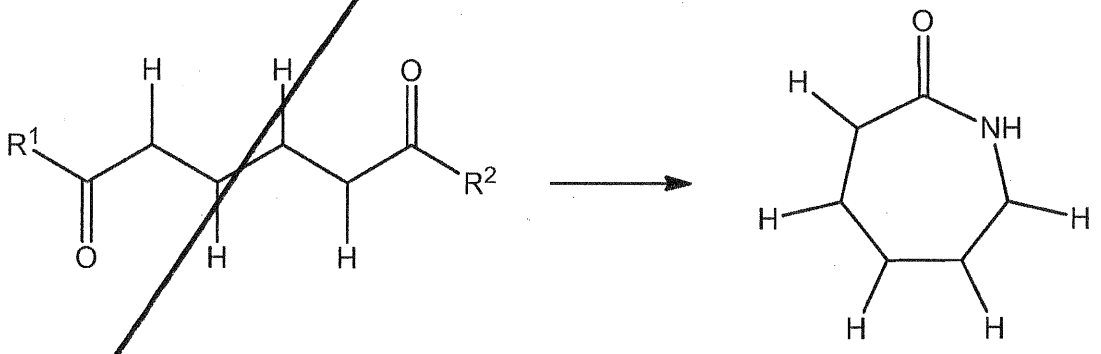
CLAIMS

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 hydroxyl, 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 claims 1 or 2, wherein reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises:

a) combining the adipic acid substrate, the ammonia, the heterogeneous catalyst, and solvent; and,

b) contacting the combined adipic acid substrate, ammonia, heterogeneous catalyst, and solvent with hydrogen.

4. The process of claims 1 or 2, wherein reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises:

a) combining the adipic acid substrate, ammonia, and solvent; and,

b) contacting the combined adipic acid substrate, ammonia, and solvent with a heterogeneous catalyst and hydrogen.

5. The process of claims 1 or 2, wherein reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and a solvent comprises:

a) combining the adipic acid substrate, ammonia, solvent, and heterogeneous catalyst at a temperature between room temperature and about 200°C; and

b) contacting with hydrogen the combined adipic acid substrate, ammonia, solvent, and heterogeneous catalyst.

6. The process of claims 1 or 2, wherein reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises:

a) contacting the heterogeneous catalyst with hydrogen;

b) adding the adipic acid substrate, the ammonia, and the solvent to the heterogeneous catalyst contacted with hydrogen.

7. The process of claims 1 or 2, wherein reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises:

a) contacting the heterogeneous catalyst with solvent at a temperature in the range of from about room temperature to about 200°C; and

b) contacting the heterogeneous catalyst and solvent with the adipic acid substrate, ammonia, and hydrogen.

8. The process of claims 1 or 2, wherein reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises:

a) contacting the adipic acid substrate with water; and,

b) contacting the adipic acid substrate and water with solvent, ammonia, hydrogen, and catalyst.

9. The process of claims 1 or 2, wherein reacting the adipic acid substrate with hydrogen and ammonia in the presence of the heterogeneous catalyst and solvent comprises:

a) combining the adipic acid substrate with water and ammonia; and,

b) contacting the combination with hydrogen, solvent, and the catalyst.

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 and 3-10, wherein the adipic acid substrate is selected from the group consisting of adipic acid, a mono-ester of adipic acid, a di-ester of adipic acid, a mono-amide of adipic acid, and a di-amide of adipic acid, or salts thereof.

12. The process of any one of claims 1-11, wherein the heterogeneous catalyst comprises ruthenium.

13. The process of any one of claims 1-12, wherein the heterogeneous catalyst comprises a first metal and a second metal, wherein the first metal is Ru and the second metal is selected from the group consisting of Fe, Co, Ni, Cu, W, and Re.

14. The process of any one of claims 1-13, 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 in any of a) or b).

20. The process of claim 13, wherein the molar ratio of first metal 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 any one of claims 1-23, 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:

converting caprolactam produced at least in part from the process of any one of claims 1-26 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 useful for the production of caprolactam comprising ruthenium and rhenium on a support comprising at least one of titania or zirconia.

35. The catalyst of claim 34 wherein the support comprises titania.

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

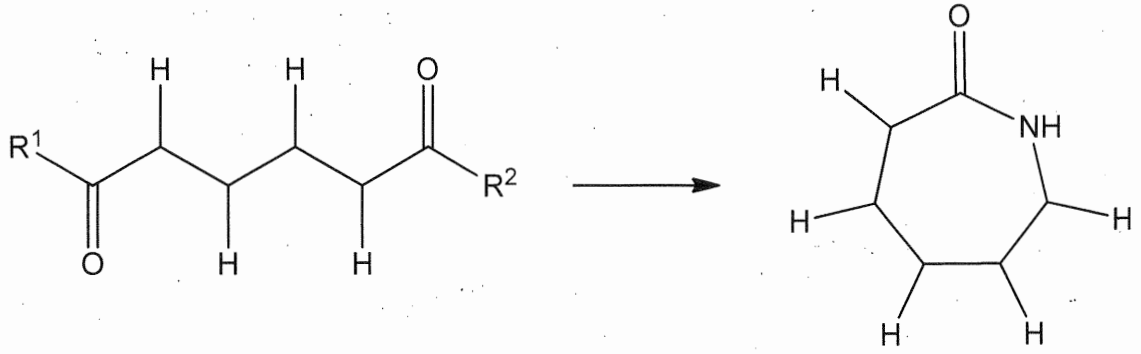
CLAIMS

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.