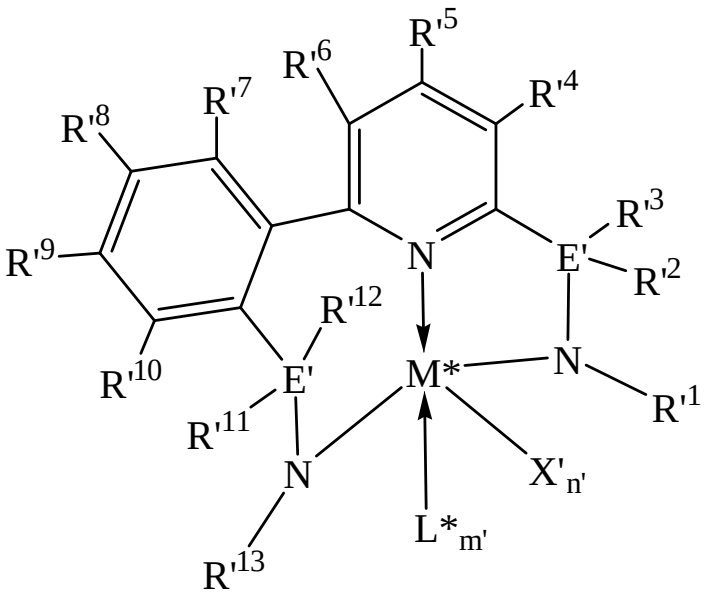
CLAIMS

What is claimed is:

1. A process to polymerize olefins comprising:

i) contacting olefins with a catalyst system comprising: 1) support comprising an organoaluminum treated layered silicate and inorganic oxide and 2) pyridyldiamido compound represented by the Formula (A):



(A)

wherein:

M* is a Group 4 metal;

each E' group is carbon;

each X' is an anionic leaving group;

L* is a neutral Lewis base;

R'^{1} and R'^{13} are independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups;

R'^{2}, R'^{3}, R'^{4}, R'^{5}, R'^{6}, R'^{7}, R'^{8}, R'^{9}, R'^{10}, R'^{11}, and R'^{12} are independently selected from the group consisting of hydrogen and hydrocarbyls ;

n' is 1 or 2;

m' is 0, 1, or 2; and

two X' groups may be joined together to form a dianionic group;

two L* groups may be joined together to form a bidentate Lewis base;

an X' group may be joined to an L* group to form a monoanionic bidentate group;

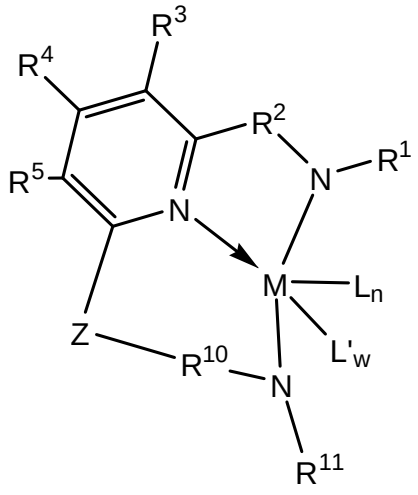
R'^{7} and R'^{8} may be joined to form a ring; and

R'^{10} and R'^{11} may be joined to form a ring; and

ii) obtaining a polyolefin composition, A, having an Mw of 1,000,000 g/mol or more and comprising 5 wt% or less of the layered silicate, where the polyolefin composition A has: 1) no diffraction peak resulting from interlamellar spacing of the organoaluminum treated layered silicate, or 2) a diffraction peak resulting from interlamellar spacing of the organoaluminum treated layered silicate of Z Angstroms or more, where Z = 5X, where X is the diffraction peak resulting from interlamellar spacing of the support before combination with the catalyst compound, as measured by wide angle x-ray scattering; where the polyolefin is an ethylene homopolymer, or an ethylene copolymer having from 0.5 wt% to 20 wt% of one or more C_3 to C_{40} olefin comonomer and a Mw/Mn of between 1 to 5.

2. A process to polymerize olefins comprising:

i) contacting olefins with a catalyst system comprising: 1) support comprising an organoaluminum treated layered silicate and inorganic oxide and 2) pyridyldiamido compound represented by the Formula (I):



(I)

wherein:

M is a Group 4 metal;

Z is $-(R^{14})_pC-C(R^{15})_q-$,

where R^{14} and R^{15} are independently selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, and wherein adjacent R^{14} and R^{15} groups may be joined to form an aromatic or saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings,

p is 1, or 2, and

q is 1, or 2;

R^1 and R^{11} are independently selected from the group consisting of hydrocarbyls and substituted hydrocarbyls;

R^2 and R^{10} are each, independently, -E(R^{12})(R^{13})- with E being carbon, and each R^{12} and R^{13} being independently selected from the group consisting of hydrogen and hydrocarbyls, R^{12} and R^{13} may be joined to each other or to R^{14} or R^{15} to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R^{12} and R^{13} may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;

R^3, R^4, and R^5 are independently selected from the group consisting of hydrogen, hydrocarbyls (such as alkyls and aryls), substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^3 & R^4 and /or R^4 & R^5) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

n is 1, or 2;

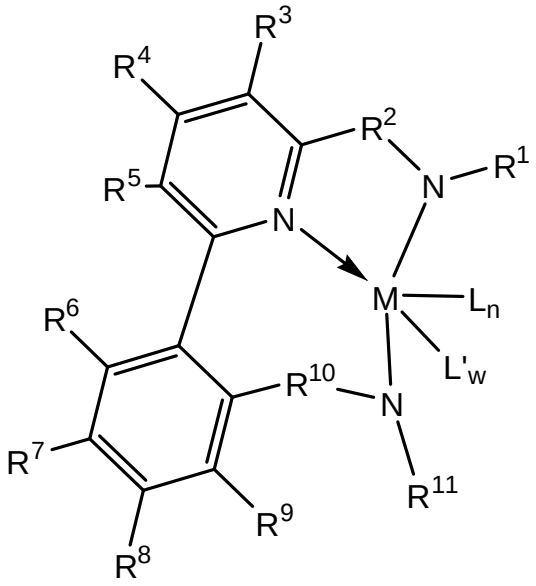
L' is a neutral Lewis base; and

w is 0, 1, or 2; and

ii) obtaining a polyolefin composition, A, having an Mw of 1,000,000 g/mol or more and comprising 5 wt% or less of the layered silicate, where polyolefin composition A has: 1) no diffraction peak resulting from interlamellar spacing of the organoaluminum treated layered silicate, and/or 2) a diffraction peak resulting from interlamellar spacing of the organoaluminum treated layered silicate of Z Angstroms or more, where Z = 5X, where X is the diffraction peak resulting from interlamellar spacing of the support before combination with the catalyst compound, as measured by wide angle x-ray scattering; where the polyolefin is an ethylene homopolymer, or an ethylene copolymer having from 0.5 wt% to 20 wt% of one or more C_3 to C_{40} olefin comonomer and a Mw/Mn of between 1 to 5.

3. A process to polymerize olefins comprising:

i) contacting olefins with a catalyst system comprising: 1) support comprising an organoaluminum treated layered silicate and inorganic oxide and 2) the pyridylamido compound is represented by the Formula II:



(II)

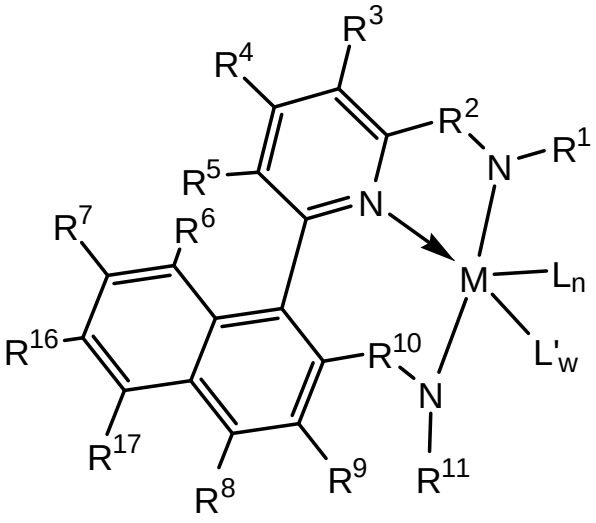
wherein:

R^6, R^7, R^8, and R^9 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^6&R^7 and/or R^7&R^8 and/or R^8&R^9, and/or R^9&R^{10}) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings; and

M, L, L', w, n, R^1, R^2, R^3, R^4, R^5, R^{10}, and R^{11} are as defined in claim 2.

4. A process to polymerize olefins comprising:

i) contacting olefins with a catalyst system comprising: 1) support comprising an organoaluminum treated layered silicate and inorganic oxide and 2) the pyridylamido compound is represented by the Formula III:



(III)

wherein:

R^6, R^7, R^8, R^9, R^{16}, and R^{17} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, wherein adjacent R groups (R^6 & R^7 and/or R^7 & R^{16} and/or R^{16} & R^{17}, and/or R^8 & R^9) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings; and

M, L, L', w, n, R^1, R^2, R^3, R^4, R^5, R^{10}, and R^{11} are as defined in claim 2.

5. The process of claim 2 or 3, wherein M is zirconium or hafnium.

6. The process of claim 1, wherein M* is hafnium.

7. The process of any of claims 2 to 5, wherein each of R^1, R^3, R^4, R^5, and R^{11} is, independently, hydrogen or a hydrocarbyl.

8. The process of any of claims 1 to 7, wherein the combination of layered silicate and inorganic oxide is spray dried prior to contact with the organoaluminum.

9. The process of claim 8, wherein the support is obtained by spray drying an aqueous slurry of alkylaluminum treated layered silicate and a Group 1 or 2 silicate.

10. The process of claim 8, wherein the support is obtained by spray drying an aqueous

slurry of trialkyl aluminum treated montmorillonite, where the alkyl is a C1 to C12 alkyl group, and a sodium, potassium, lithium, or magnesium silicate, or a mixture thereof.

11. The process of any of claims 1 to 10, wherein the support comprises spheroidal particles of the combination of the organoaluminum treated layered silicate and the inorganic oxide.

12. The process of any of claims 1 to 11, wherein the support comprises particles having: 1) an average diameter of 20 to 100 microns, and/or 2) a pore volume of between 0.1 and 0.4 cc/g; and/or 3) a surface area of between 100 and 200 m^2/g.

13. The process of any of claims 1 to 12, wherein the support comprises at least 10 wt% montmorillonite, preferably from 50 to 90 wt% montmorillonite, based upon the weight of the organoaluminum treated layered silicate and the inorganic oxide.

14. The process of any of claims 1 to 13, wherein the organoaluminum comprises trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-iso-octylaluminum, triphenylaluminum, or a combination thereof.

15. The process of any of claims 1 to 14, wherein the polyolefin has a bulk density of 0.25 g/ml.

16. The process of any of claims 1 to 15, wherein the polyolefin has no diffraction peak resulting from interlamellar spacing of the organoaluminum treated layered silicate.

17. The process of any of claims 1 to 16, wherein the polyolefin is an ethylene polymer.

18. The process of any of claims 1 to 17, wherein the polyolefin has an Mw from 1,000,000 to 3,000,000 g/mol.

19. The process of any of claims 1 to 18, wherein the polymerization is conducted in the gas phase or the slurry phase.

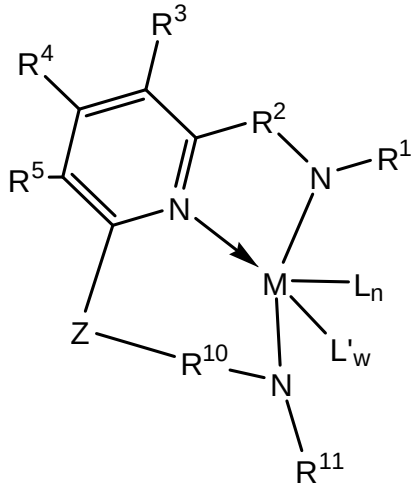
20. The process of any of claims 1 to 19, wherein the support comprising an organoaluminum treated layered silicate support and inorganic oxide has an aspect ratio of 1 to 1.7.

21. The process of any of claims 1 to 20, wherein the catalyst system has an average aspect ratio of 1 to 1.7.

22. An ethylene polymer having an Mw of 1,000,000 g/mol or more and comprising 0.1 to 5 wt% of a layered silicate, where the ethylene polymer has no diffraction peak resulting from interlamellar spacing of the layered silicate, as measured by wide angle x-ray scattering.

23. An ethylene polymer having an Mw of 1,000,000 g/mol or more and comprising 0.1 to 5 wt% of a layered silicate derived from a supported catalyst used to produce the ethylene polymer, where the ethylene polymer has 1) no diffraction peak resulting from interlamellar spacing of the layered silicate present in the supported catalyst, or 2) a diffraction peak resulting from interlamellar spacing of the layered silicate of Z Angstroms or more, where Z = 5X, where X is the diffraction peak resulting from interlamellar spacing of the layered silicate present in the supported catalyst, as measured by wide angle x-ray scattering.

24. A catalyst system comprising: 1) support comprising an organoaluminum treated layered silicate and inorganic oxide and 2) pyridyldiamido compound represented by the Formula (I):

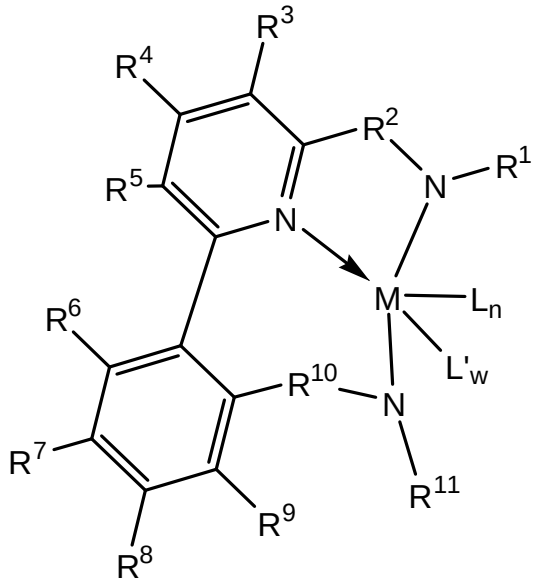


(I)

wherein:

M is a Group 4 metal;
Z is $-(R^{14})_pC-C(R^{15})_q-$,
where R^{14} and R^{15} are independently selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, and wherein adjacent R^{14} and R^{15} groups may be joined to form an aromatic or saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings,
p is 1, or 2, and
q is 1, or 2;
R^1 and R^{11} are independently selected from the group consisting of hydrocarbyls and substituted hydrocarbyls;
R^2 and R^{10} are each, independently, $-E(R^{12})(R^{13})-$ with E being carbon, and each R^{12} and R^{13} being independently selected from the group consisting of hydrogen and hydrocarbyls, R^{12} and R^{13} may be joined to each other or to R^{14} or R^{15} to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R^{12} and R^{13} may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;
R^3, R^4, and R^5 are independently selected from the group consisting of hydrogen, hydrocarbyls (such as alkyls and aryls), substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^3 & R^4 and /or R^4 & R^5) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;
L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;
n is 1, or 2;
L' is a neutral Lewis base; and
w is 0, 1, or 2.

25. A catalyst system comprising: 1) support comprising an organoaluminum treated layered silicate and inorganic oxide and 2) the pyridylamido compound is represented by the Formula II:



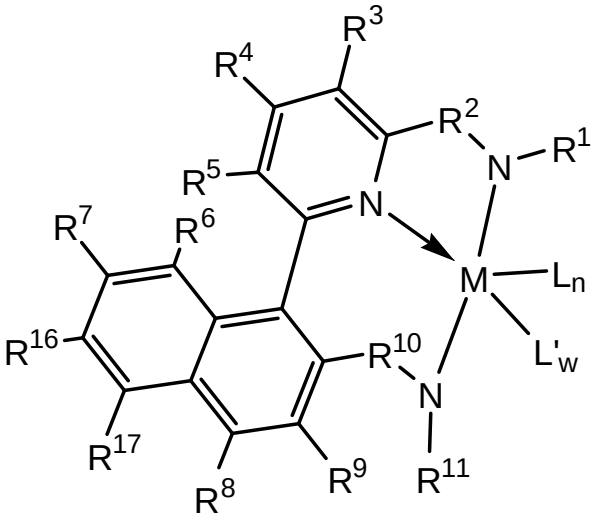
(II)

wherein:

R^6, R^7, R^8, and R^9 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^6&R^7 and/or R^7&R^8 and/or R^8&R^9, and/or R^9&R^{10}) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings; and

M, L, L', w, n, R^1, R^2, R^3, R^4, R^5, R^{10}, and R^{11} are as defined in claim 24.

26. A catalyst system comprising: 1) support comprising an organoaluminum treated layered silicate and inorganic oxide and 2) the pyridylamido compound is represented by the Formula III:



(III)

wherein:

R^6, R^7, R^8, R^9, R^{16}, and R^{17} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, wherein adjacent R groups (R^6 & R^7 and/or R^7 & R^{16} and/or R^{16} & R^{17}, and/or R^8 & R^9) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings; and

M, L, L', w, n, R^1, R^2, R^3, R^4, R^5, R^{10}, and R^{11} are as defined in claim 24.

27. The catalyst system of claim 24 or 25, wherein M is zirconium or hafnium.

28. The catalyst system of claim 23, wherein M* is hafnium.

29. The catalyst system of any of claims 24 to 28, wherein each of R^1, R^3, R^4, R^5, and R^{11} is, independently, hydrogen or a hydrocarbyl.

30. The catalyst system of any of claims 23 to 29, wherein the combination of layered silicate and inorganic oxide is spray dried prior to contact with the organoaluminum.

31. The catalyst system of claim 30, wherein the support is obtained by spray drying an aqueous slurry of alkylaluminum treated layered silicate and a Group 1 or 2 silicate.

32. The catalyst system of claim 30, wherein the support is obtained by spray drying an

aqueous slurry of trialkyl aluminum treated montmorillonite, where the alkyl is a C1 to C12 alkyl group, and a sodium, potassium, lithium, or magnesium silicate, or a mixture thereof.

33. The catalyst system of any of claims 23 to 32, wherein the support comprises spheroidal particles of the combination of the organoaluminum treated layered silicate and the inorganic oxide.

34. The catalyst system of any of claims 23 to 33, wherein the support comprises particles having: 1) an average diameter of 20 to 100 microns, and/or 2) a pore volume of between 0.1 and 0.4 cc/g; and/or 3) a surface area of between 100 and 200 m^2/g.

35. The catalyst system of any of claims 23 to 34, wherein the support comprises at least 10 wt% montmorillonite, preferably from 50 to 90 wt% montmorillonite, based upon the weight of the organoaluminum treated layered silicate and the inorganic oxide.

36. The catalyst system of any of claims 23 to 35, wherein the organoaluminum comprises trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-iso-octylaluminum, triphenylaluminum, or a combination thereof.

37. The catalyst system of any of claims 23 to 36, wherein the polymerization is conducted in the gas phase or the slurry phase.

38. The catalyst system of any of claims 23 to 37, wherein the support comprising an organoaluminum treated layered silicate support and inorganic oxide has an aspect ratio of 1 to 1.7.

39. The catalyst system of any of claims 23 to 38, wherein the catalyst system has an average aspect ratio of 1 to 1.7.