CLAIMS

1. A process to produce a fluorided solid oxide, the process comprising:

(a) calcining a solid oxide at a peak calcining temperature to produce a calcined solid oxide; and

(b) contacting the calcined solid oxide at a peak fluoriding temperature with a vapor comprising a fluorine-containing compound to produce the fluorided solid oxide;

wherein the peak fluoriding temperature is at least about 50 °C less than the peak calcining temperature.

2. The process of claim 1, wherein:

the peak calcining temperature is in a range from about 500 °C to about 1000 °C;

the peak fluoriding temperature is in a range from about 350 °C to about 650 °C;

the peak fluoriding temperature is from about 60 °C to about 600 °C less than the peak calcining temperature; or

any combination thereof.

3. The process of claim 1, wherein:

the peak calcining temperature is in a range from about 600 °C to about 750 °C;

the peak fluoriding temperature is in a range from about 400 °C to about 600 °C;

the peak fluoriding temperature is from about 75 °C to about 400 °C less than the peak calcining temperature; or

any combination thereof.

4. The process of claim 1, wherein:

the fluorine-containing compound comprises perfluorohexane, perfluoroacetic anhydride, tetrafluoroethane, or a combination thereof;

the fluorided solid oxide comprises fluorided alumina, fluorided silica-alumina, fluorided silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, or a combination thereof; or

both.

5. The process of claim 1, wherein the fluorine-containing compound comprises a fluorocarbon.

6. The process of claim 1, wherein the solid oxide comprises silica, alumina, titania, zirconia, magnesia, boria, silica-alumina, silica-coated alumina, silica-titania, silica-zirconia, alumina-boria, or any combination thereof.

7. The process of claim 6, wherein the fluorided solid oxide comprises fluorided silica-alumina, fluorided silica-coated alumina, fluorided alumina, or a combination thereof.

8. The process of claim 1, wherein step (a) and step (b) are performed in an oxidizing atmosphere.

9. The process of claim 1, wherein:

the fluorided solid oxide comprises from about 5 to about 12 wt. % fluorine, based on the weight of the fluorided solid oxide;

the vapor comprises from about 100 ppmv to about 20 volume % fluorine-containing compound; or

both.

10. The process of claim 1, wherein:

the contacting in step (b) is performed for a time period of less than about 8 hr; and

the fluorine-containing compound is present in the vapor for less than about 15 min.

11. The process of claim 1, wherein the fluorided solid oxide has:

a pore volume in a range from about 1.2 to about 2 mL/g; and

a surface area in a range from about 275 to about 700 m^2/g.

12. The process of claim 1, wherein the surface area of the fluorided solid oxide produced by the process is at least about 5% greater than a surface area of a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature.

13. The process of claim 1, wherein the catalyst activity of a catalyst system containing the fluorided solid oxide produced by the process is at least about 5% greater than that of a catalyst system containing a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature.

14. A fluorided solid oxide produced by the process of claim 1.

15. A catalyst composition comprising a transition metal compound and the fluorided solid oxide of claim 14.

16. A polymerization process comprising contacting the catalyst composition of claim 15 with an olefin monomer and optionally an olefin comonomer under polymerization conditions to produce an olefin polymer.

17. A process to produce a fluorided solid oxide, the process comprising:

(a) calcining a solid oxide at a peak calcining temperature in an oxidizing atmosphere to produce a calcined solid oxide; and

(b) contacting the calcined solid oxide at a peak fluoriding temperature with a vapor comprising a fluorine-containing compound and oxygen to produce the fluorided solid oxide;

wherein the peak fluoriding temperature is from about 50 °C to about 600 °C less than the peak calcining temperature.

18. The process of claim 17, wherein:

the peak calcining temperature is in a range from about 550 °C to about 900 °C;

the peak fluoriding temperature is in a range from about 350 °C to about 650 °C; and

the peak fluoriding temperature is from about 75 °C to about 300 °C less than the peak calcining temperature.

19. The process of claim 17, wherein:

the fluorine-containing compound comprises perfluorohexane, perfluoroacetic anhydride, tetrafluoroethane, or a combination thereof; and

the fluorided solid oxide comprises fluorided silica-alumina, fluorided silica-coated alumina, fluorided alumina, or a combination thereof.

20. The process of claim 17, wherein:

the surface area of the fluorided solid oxide produced by the process is from about 5% to about 15% greater than a surface area of a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature; and

the catalyst activity of a catalyst system containing the fluorided solid oxide produced by the process is at least about 10% greater than that of a catalyst system containing a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature.

CLAIMS

We claim:

1. A process to produce a fluorided solid oxide, the process comprising:

(a) calcining a solid oxide at a peak calcining temperature to produce a calcined solid oxide; and

(b) contacting the calcined solid oxide at a peak fluoriding temperature with a vapor comprising a fluorine-containing compound to produce the fluorided solid oxide;

wherein the peak fluoriding temperature is at least about 50° C. less than the peak calcining temperature, and

wherein the surface area of the fluorided solid oxide produced by the process is at least about 5% greater than a surface area of a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature.

2. The process of claim 1, wherein:

the peak calcining temperature is in a range from about 500° C. to about 1000° C.;

the peak fluoriding temperature is in a range from about 350° C. to about 650° C.;

the peak fluoriding temperature is from about 60° C. to about 600° C. less than the peak calcining temperature; or

any combination thereof.

3. The process of claim 1, wherein:

the peak calcining temperature is in a range from about 600° C. to about 750° C.;

the peak fluoriding temperature is in a range from about 400° C. to about 600° C.;

the peak fluoriding temperature is from about 75° C. to about 400° C. less than the peak calcining temperature; or

any combination thereof.

4. The process of claim 1, wherein:

the fluorine-containing compound comprises perfluorohexane, perfluoroacetic anhydride, tetrafluoroethane, or a combination thereof; and/or

the fluorided solid oxide comprises fluorided alumina, fluorided silica-alumina, fluorided silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, or a combination thereof.

5. The process of claim 1, wherein the fluorine-containing compound comprises a fluorocarbon.

6. The process of claim 1, wherein the solid oxide comprises silica, alumina, titania, zirconia, magnesia, boria, silica-alumina, silica-coated alumina, silica-titania, silica-zirconia, alumina-boria, or any combination thereof.

7. The process of claim 6, wherein the fluorided solid oxide comprises fluorided silica-alumina, fluorided silica-coated alumina, fluorided alumina, or a combination thereof.

8. The process of claim 1, wherein step (a) and step (b) are performed in an oxidizing atmosphere.

9. The process of claim 1, wherein:

the fluorided solid oxide comprises from about 5 to about 12 wt. % fluorine, based on the weight of the fluorided solid oxide; and/or

the vapor comprises from about 100 ppmv to about 20 volume % fluorine-containing compound.

10. The process of claim 1, wherein:

the contacting in step (b) is performed for a time period of less than about 8 hr; and

the fluorine-containing compound is present in the vapor for less than about 15 min.

11. The process of claim 1, wherein the fluorided solid oxide has:

a pore volume in a range from about 1.2 to about 2 mL/g; and

a surface area in a range from about 275 to about 700 m^2/g.

12. The process of claim 1, wherein the catalyst activity of a catalyst system containing the fluorided solid oxide produced by the process is at least about 5% greater than that of a catalyst system containing a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature.

13. A fluorided solid oxide produced by the process of claim 1.

14. A catalyst composition comprising a transition metal compound and the fluorided solid oxide of claim 13.

15. A polymerization process comprising contacting the catalyst composition of claim 14 with an olefin monomer and optionally an olefin comonomer under polymerization conditions to produce an olefin polymer.

16. A process to produce a fluorided solid oxide, the process comprising:

(a) calcining a solid oxide at a peak calcining temperature in an oxidizing atmosphere to produce a calcined solid oxide; and

(b) contacting the calcined solid oxide at a peak fluoriding temperature with a vapor comprising a fluorine-containing compound and oxygen to produce the fluorided solid oxide;

wherein the peak fluoriding temperature is from about 50° C. to about 600° C. less than the peak calcining temperature, and

wherein the surface area of the fluorided solid oxide produced by the process is at least about 5% greater than a surface area of a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature.

17. The process of claim 16, wherein:

the peak calcining temperature is in a range from about 550° C. to about 900° C.;

the peak fluoriding temperature is in a range from about 350° C. to about 650° C.; and

the peak fluoriding temperature is from about 75° C. to about 300° C. less than the peak calcining temperature.

18. The process of claim 16, wherein:

the fluorine-containing compound comprises perfluorohexane, perfluoroacetic anhydride, tetrafluoroethane, or a combination thereof; and

the fluorided solid oxide comprises fluorided silica-alumina, fluorided silica-coated alumina, fluorided alumina, or a combination thereof.

19. The process of claim 16, wherein:

the surface area of the fluorided solid oxide produced by the process is from about 5% to about 15% greater than a surface area of a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature; and

the catalyst activity of a catalyst system containing the fluorided solid oxide produced by the process is at least about 10% greater than that of a catalyst system containing a fluorided solid oxide obtained by performing the contacting step at the peak calcining temperature.