[0010] It is to the production of such improved silica supported-titania substrates, and catalysts made therefrom, that the present techniques are directed.

[0010a] The invention is defined in the independent claims. Some optional features are defined in the dependent claims.

SUMMARY OF THE DISCLOSURE

[0011] The present disclosure describes compositions and processes for the production of stable ultrafine anatase titania for use, for example, as a support material for vanadia catalysts preferably for use in a catalytic emission control system. The stabilization involves treatment of the titania with a soluble, low molecular weight form and/or small nanoparticle form (< 5 nm) of silica such as, in a preferred embodiment, a tetra(alkyl)ammonium silicate, such as tetramethylammonium silicate, or silicic acid, which serves to efficiently maintain the anatase phase and prevent sintering (crystal growth) under severe thermal and hydrothermal conditions, even in the presence of vanadia. The novel silica-stabilized titanias combined with vanadia have equal or improved catalytic activity for selective catalytic reduction of NOx compared to currently-available silicatitania based vanadia catalysts.

[0012] In one of its aspects, a catalyst support material which comprises anatase titania particles comprising ≥ 85 wt% dry weight of TiO_2 and ≤ 10 wt% dry weight of SiO_2, wherein the SiO_2 is substantially in a low molecular weight and/or small nanoparticle form, is described. The catalyst support material may further comprise, for example, 3% to 10% WO_3 and may have a BET surface area of at least 80 m^2/gm. The catalyst support material may comprise ≥ 85% dry weight Of TiO_2, 3% - 9% of SiO_2, and 3% - 9% dry weight of WO_3 ,for example. The SiO_2 is present at a fractional monolayer value of less than 1.0 before the catalyst support material is sintered. The small nanoparticle form of the SiO_2 comprises a diameter of <5nm. The low molecular weight form of the SiO_2 comprises a MW of < 100,000. The SiO_2 may comprise silicon atoms which are substantially (e.g., >50%) in the Q^3, Q^2, Q^1 and Q^0 coordination environments. The SiO_2 may comprise patches which are substantially ≤ 5 nm deep after redistribution as seen by scanning electron microscopy or by transmission electron microscopy. The TiO_2 used may optionally not be prepared in the presence of urea.

[0013] In another aspect, the catalyst may be a vanadia catalyst

not produced in the presence of urea. The small nanoparticle form of the SiO_2 of the silica precursor solution may substantially comprise a diameter of < 5 nm. The low molecular weight form of the SiO_2 of the silica precursor solution may substantially comprise a MW of < 100,000. The SiO_2 of the silica precursor solution may comprise silicon atoms which are substantially (e.g. >50%) in the Q^3, Q^2, Q^1 and Q^0coordination environments. The silica precursor solution may comprise a tetra(alkyl)ammonium silicate solution or silicic acid. The SiO_2 may substantially comprise patches which are ≤5 nm in depth after redistribution as seen by scanning electron microscopy or by transmission electron microscopy. The method may further comprise combining the TiO_2-WO_3-SiO_2 mixture with V_2O_5 to form a vanadia catalyst. The vanadia catalyst thus formed may comprise, for example, 0.5% to 3% to 5% dry weight of V_2O_5. The V_2O_5 thereof may be present at a fractional monolayer value of less than 1.0 before sintering. The vanadia catalyst may be sintered at ≥ 650°C for example.

[0016] In another aspect, a method of producing the above mentioned silica-stabilized titania catalyst support material by providing a TiO_2 slurry comprising TiO_2 particles, providing a particulate silica source, combining the TiO_2 slurry with the particulate silica source to form a TiO_2-SiO_2 mixture, and adjusting the TiO_2-SiO_2 mixture to a pH <8.5 and a temperature <80°C wherein the particulate silica source is dissolved and reprecipitated on the TiO_2 particles to form the silica-stabilized titania catalyst support material is contemplated. The method may further comprise the step of combining the silica-stabilized titania catalyst support material with WO_3 to form a silica-stabilized titania tungsten catalyst support material. The method may further comprise washing and sintering the silica-stabilized titania tungsten catalyst support material. The silica-stabilized titania tungsten catalyst support material may comprise, for example, 86%-94% dry weight of TiO_2, 3%-9% dry weight of a SiO_2, and 3%-7% dry weight of WO_3, and the titania support material may primarily comprise a surface area of at least 80 m^2/gm before sintering. The TiO_2 particles of the TiO_2 slurry may comprise, for example, preformed titanium hydroxide, titanium oxy-hydroxide or titanium dioxide particles. The TiO_2 particles of the TiO_2 slurry optionally are not produced in the presence of urea. The SiO_2 of the TiO_2-SiO_2 mixture, after dissolving, may comprise silicon atoms which are

silica particle with a diameter of 5 nm has 1500 silicate atoms, and 37% of these silicate atoms are on the particle surface, whereas a particle of 1 nm has almost all the silicate atoms on the surface. Thus, it may be desirable to use silica sources which substantially comprise particles which have diameters <5 nm and/or which have low molecular weights for example wherein the MW < 100,000, and hence are available for interaction with the titania. An exception, as will be described below, involves subsequent modification of particulate silica using conditions of pH and temperature wherein the particle silica has been dissolved and re-precipitated onto the titania surface.

[0042] Where used herein the term "substantially" is intended to mean that more than 50% of the process or material in question has the particular characteristic or condition to which is being referred.

[0043] For example, as noted above, in the present invention the catalyst support material, in a preferred embodiment comprises silica which is substantially in a low molecular weight form and/or a small nanoparticle form. By this is meant that over 50% of the silica is either in the low molecular weight form (MW < 100,000) or in a small nanoparticle from (diameter < 5 nm), or is a combination of both. In a more preferred version the silica comprises > 60% low molecular weight forms and/or small nanoparticle forms. In a still more preferred version the silica comprises > 70% low molecular weight and/or small nanoparticle forms. In a still more preferred version the silica comprises > 80%, and yet still more preferred, > 90%, low molecular weight forms and/or small nanoparticle forms of silica.

[0044] Furthermore, the low molecular weight and small nanoparticle forms preferably have geometric surface areas of > 450 m^2/g.

[0045] Particulate forms of silica (i.e., wherein diameter is > 5 nm) include silica gel, precipitated silica and fumed silica. While the primary particles of dense, amorphous silica in these particulate forms can be very small (e.g., 2.5 nm), the primary particles are irreversibly agglomerated together to form much larger secondary particles that can range in size from hundreds of nanometers to many microns in diameter. These secondary particles obviously do not have a large portion of the silicate

What is claimed is:

1. A catalyst support material, comprising:

anatase titania particles comprising ≥ 85 wt% and < 100 wt% dry weight of TiO_2, and > 0 wt% and ≤ 10 wt% dry weight of SiO_2, wherein the SiO_2 is in a form selected from the group consisting of: low molecular weight oligomers having a molecular weight < 100,000, nanoparticles with a diameter of < 5 nm, and combinations thereof, and is present at a fractional monolayer value of less than 1.0 before the catalyst support material is sintered; and wherein the catalyst support material is useful for catalytic NO_x reduction.

2. The catalyst support material of claim 1, further comprising 3% to 10% dry weight WO_3.

3. The catalyst support material of claim 2, wherein the BET surface area is at least 80 m^2/gm.

4. The catalyst support material of claim 1, comprising ≥ 85% dry weight of TiO_2, 3%-9% of SiO_2, and 3%-9% dry weight of WO_3.

5. The catalytic support material of claim 1, wherein at least 50% of the silicon atoms of the SiO_2 are in the Q^3, Q^2, Q^1 and Q^0 coordination environments.

6. The catalytic support material of claim 1, wherein the SiO_2 comprises patches which are ≤ 5 nm deep after redistribution as seen by scanning electron microscopy or by transmission electron microscopy.

7. The catalytic support material of claim 1, wherein the TiO_2 was not prepared in the presence of urea.

8. A vanadia catalyst, comprising:

the catalyst support material of claim 2, having V_2O_5 disposed thereon.

9. The vanadia catalyst of claim 8, comprising 0.5%-5% dry weight of V_2O_5.

10. The vanadia catalyst of claim 8, wherein the V_2O_5 thereof is present at a fractional monolayer value of less than 1.0 before sintering.

11. The vanadia catalyst of claim 8, which has been sintered at ≥ 650 °C.

12. A diesel emission catalytic device comprising the vanadia catalyst of claim 8.

13. A diesel emission control system, comprising:

the diesel emission catalytic device of claim 12; and

a diesel particulate filter, and wherein the diesel emission catalytic device is positioned upstream of or downstream of the diesel particulate filter.

14. A method of catalyzing the conversion of nitrogen oxides to N_2 gas, comprising:

exposing engine emissions comprising NO_x to the vanadia catalyst of claim 8, with an added reductant to produce N_2 and H_2O.

15. The method of claim 14, wherein the reductant is NH_3 and/or urea.

16. The method of claim 14, wherein the vanadia catalyst comprises 0.5%-3% dry weight of V_2O_5.

17. The method of claim 14, wherein the engine emissions are passed through a diesel particulate filter before or after being exposed to the vanadia catalyst.

18. A method of producing a catalyst support material, comprising:

providing a slurry comprising TiO_2;

combining the TiO_2 slurry with (1) a silica precursor solution comprising SiO_2,

wherein the SiO_2 is in a form selected from the group consisting of: low molecular weight oligomers having a molecular weight < 100,000, nanoparticles with a diameter of< 5 nm, and combinations thereof, and with (2) WO_3 to form a TiO_2-WO_3-SiO_2 mixture; wherein the silica precursor solution is combined with the TiO_2 slurry before, after, or

while the WO_3 is combined with the TiO_2 slurry; and washing and sintering the TiO_2-WO_3-SiO_2 mixture to form a silica-stabilized titania support material.

19. The method of claim 18, wherein the silica-stabilized titania support material comprises:

86%-94% dry weight of TiO_2, 3%-9% dry weight of a SiO_2, and 3%-7% dry weight of WO_3;

and wherein the titania support material primarily comprises a surface area of at least 80 m^2/gm before sintering.

20. The method of claim 18, wherein the TiO_2 of the slurry comprise preformed titanium hydroxide, titanium oxy-hydroxide or titanium dioxide particles.

21. The method of claim 18, wherein the TiO_2 of the slurry is not produced in the presence of urea.

22. The method of claim 18, wherein at least 50% of the silicon atoms of the silica precursor solution are in the Q^3, Q^2, Q^1 and Q^0 coordination environments.

23. The method of claim 18, wherein the silica precursor solution comprises a tetra(alkyl)ammonium silicate solution or silicic acid.

24. The method of claim 18, wherein the SiO_2 comprises patches which are ≤5 nm in depth after redistribution as seen by scanning electron microscopy or by transmission electron microscopy.

25. The method of claim 18, comprising combining the TiO_2-WO_3-SiO_2 mixture with V_2O_5 to form a vanadia catalyst.

26. The method of claim 25, wherein the vanadia catalyst comprises 0.5%-3% dry weight of V_2O_5.

27. The method of claim 25, wherein the V_2O_5 of the vanadia catalyst is present at a fractional monolayer value of less than 1.0 before sintering.

28. The method of claim 25, comprising the additional step of sintering the vanadia catalyst at ≥ 650 °C.

29. A method of producing the catalyst support material of claim 1, comprising:

providing a TiO_2 slurry comprising TiO_2 particles;

providing a particulate silica source;

combining the TiO_2 slurry with the particulate silica source to form a TiO_2-SiO_2 mixture; and

adjusting the TiO_2-SiO_2 mixture to a pH < 8.5 and a temperature < 80 °C, wherein the particulate silica source is dissolved and re-precipitated on the TiO_2 particles to form a silica-stabilized titania catalyst support material.

30. The method of claim 29, further comprising the step of combining the silica-stabilized titania catalyst support material with WO_3 to form a silica-stabilized titania tungsten catalyst support material.

31. The method of claim 30, further comprising washing and sintering the silica-stabilized titania tungsten catalyst support material.

32. The method of claim 30, wherein the silica-stabilized titania tungsten catalyst support material, comprises:

86%-94% dry weight of TiO_2, 3%-9% dry weight of a SiO_2, and 3%-7% dry weight of WO_3; and

wherein the titania support material primarily comprises a surface area of at least 80 m^2/gm before sintering.

33. The method of claim 29, wherein the TiO_2 particles of the TiO_2 slurry comprise preformed titanium hydroxide, titanium oxy-hydroxide or titanium dioxide particles.

34. The method of claim 29, wherein the TiO_2 particles of the TiO_2 slurry are not produced in the presence of urea.

35. The method of claim 29, wherein at least 50% of the silicon atoms of the TiO_2-SiO_2 mixture, after dissolving, are in the Q^3, Q^2, Q^1 and Q^0 coordination environments.

36. The method of claim 29, wherein the SiO_2 on the TiO_2 particles comprises patches which are ≤ 5 nm in depth after redistribution of the SiO_2 as seen by scanning electron microscopy or by transmission electron microscopy.

37. The method of claim 30, comprising combining the TiO_2-WO_3-SiO_2 mixture with V_2O_5 to form a vanadia catalyst.

38. The method of claim 37, wherein the vanadia catalyst comprises 0.5%-3% dry weight of V_2O_5.

39. The method of claim 37, wherein the V_2O_5 of the vanadia catalyst is present at a fractional monolayer value of less than 1.0 before sintering.

40. The method of claim 37, comprising the additional step of sintering the vanadia catalyst at ≥ 650°C.