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

## 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 silica-titania based vanadia catalysts.

**[0012]** In one of its aspects, the invention is 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. 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 $SiO_2$ may be present at a fractional monolayer value of less than 1.0 before the catalyst support material is sintered. The small nanoparticle form of the $SiO_2$ may comprise a diameter of <5nm. The low molecular weight form of the $SiO_2$ may comprise 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 invention may be a vanadia catalyst

comprising a silica-stabilized titania catalyst support material as described herein which comprises $V_2O_5$ disposed thereon. The vanadia catalyst may comprise, for example, 0.5% to 5% dry weight of $V_2O_5$ (or more preferably 1.0 to 3%). The $V_2O_5$ 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. In another aspect, the invention may be a diesel emission catalytic device comprising the vanadia catalyst as described herein. In another aspect the invention may be a diesel emission control system which comprises the diesel emission catalytic device described above and a diesel particulate filter, and wherein the diesel emission catalytic device is positioned upstream of or downstream of the diesel particulate filter.

**[0014]** In another one of its aspects, the invention is a method of catalyzing the conversion of nitrogen oxides to $N_2$ gas, comprising exposing engine emissions comprising NOx to the vanadia catalyst as described herein with an added reductant to produce $N_2$ and $H_2O$. The reductant may be for example $NH_3$ and/or urea. In the method the vanadia catalyst may comprise 0.5%-5% (or more preferably 1.0% to 3%) dry weight of $V_2O_5$, for example. The engine emissions may be passed through a diesel particulate filter before or after being exposed to the vanadia catalyst.

**[0015]** In another of its aspects, the invention is 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 $SiO_2$ substantially in a low molecular weight form and/or $SiO_2$ comprising small nanoparticles 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 then washing and sintering the $TiO_2$-$WO_3$-$SiO_2$ mixture to form a silica-stabilized titania support material. In the method the silica-stabilized titania 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 $TiO_2$ of the slurry may comprise, for example, preformed titanium hydroxide, titanium oxy-hydroxide or titanium dioxide particles. Optionally, the $TiO_2$ of the slurry is

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 $Q^0$ coordination 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, the invention contemplates a method of producing a 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. 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

substantially (e.g., > 50%) in the $Q^3$, $Q^2$, $Q^1$ and $Q^0$ coordination environments. The $SiO_2$ on the $TiO_2$ particles of the method may substantially comprise patches which are ≤5 nm in depth after redistribution of the $SiO_2$ 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. In the method, the vanadia catalyst may comprise, for example, 0.5%- 3% dry weight of $V_2O_5$. The $V_2O_5$ of the vanadia catalyst may be present at a fractional monolayer value of less than 1.0 before sintering, and the vanadia catalyst may be sintered at ≥650°C.

**[0017]** Other aspects of the invention will become evident upon consideration of the description below.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0018]** Figure 1 is a graph showing the effect of calcination temperature on surface area of vanadia catalyst.

**[0019]** Figure 2 is a graph showing the effect of calcination temperature on the percentage of anatase phase of titania in vanadia catalysts.

**[0020]** Figure 3 is a graph showing the effect of calcination temperature on DeNox activity of 1% vanadia catalysts.

**[0021]** Figure 4 is a graph showing the effect of calcination temperature on DeNOx conversion of 3% vanadia catalysts.

**[0022]** Figure 5 is a graph showing the effect of temperature on DeNOx activity of various vanadia catalysts.

**[0023]** Figure 6 is a graph showing the effect of temperature on surface area of a catalyst support of the present invention versus a conventional catalyst support.

**[0024]** Figure 7 is a transmission electron micrograph (TEM) of a silica-tungsta-titania catalyst of Example 6 showing two-dimensional patches of silica <2 nm in depth on the titania surface.

**[0025]** Figure 8 is a scanning electron micrograph of a vanadia-titania catalyst of Example 10 showing ~20 nm colloidal silica particles disposed thereon.

**[0026]** Figure 9 is a transmission electron micrograph (TEM) of a catalyst showing ~20 nm colloidal silica particles on the outer surface of the

vanadia-titania catalyst of Example 10.

**[0027]** Figure 10 is a transmission electron micrograph (TEM) of the catalytic particles of Example 11, showing anatase crystals with a patchy, two-dimensional silica layer on the outer crystal surface. In this image, no silica particles are observable.

**[0028]** Figure 11 is a transmission electron micrograph (TEM) of the catalytic particles of Example 11, showing anatase crystals with a patchy, two-dimensional silica layer on the outer crystal surface. In this image, one remnant silica particle that is <5 nm in diameter can be seen.

**[0029]** Figure 12 is a transmission electron micrograph (TEM) of the catalytic particles of Example 12, showing small, two-dimensional patches of silica on the anatase crystallites.

**[0030]** Figure 13 is a transmission electron micrograph of silica patches present on the surface of the catalytic particles of anatase titania of Example 13.

**[0031]** Figure 14 is a transmission electron micrograph of silica patches present on the surface of the catalytic particles of anatase titania of Example 13.

**[0032]** Figure 15 is a transmission electron micrograph (TEM) of the catalyst support before vanadia addition and sintering. The image shows the lattice fringes associated with anatase titania; the silica is present as 1-3 nm patches on the titania surface (Example 14).

**[0033]** Figure 16 is a transmission electron micrograph (TEM) of the vanadia catalyst that shows large (>20 nm) three dimensional silica nodules (see arrows) that are not well dispersed on the titania surface (e.g., Example 15).

**[0034]** Figure 17 is another transmission electron micrograph (TEM) of the vanadia catalyst that shows large (>20 nm) three dimensional silica nodules (see arrows) that are not well dispersed on the titania surface (e.g., Example 15).

**[0035]** Figure 18 is a graph showing the effect of various calcination (activation) temperatures on the deNOx catalytic activities of forms of titania-supported vanadium catalysts.

## DETAILED DESCRIPTION OF THE INVENTION

**[0036]** A primary goal of the present invention is production of a

stable, high surface area titania support material in anatase crystal form, primarily to be used as a support for vanadia ($V_2O_5$) in diesel emission control catalyst applications. The stabilization involves treatment of the titania with silica in a low molecular weight form and/or small nanoparticle form, such as a soluble precursor tetra(alkyl)ammonium silicate (i.e., tetramethylammonium silicate) or tetraethylorthosilicate (TEOS). Other examples of low molecular weight silica precursors which may be used in the present invention include, but are not limited to aqueous solutions of silicon halides (i.e., anhydrous $SiX_4$, where X= F, Cl, Br, or I), silicon alkoxides (i.e., $Si(OR)_4$, where R=methyl, ethyl, isopropyl, propyl, butyl, iso-butyl, sec-butyl, tert-butyl, pentyls, hexyls, octyls, nonyls, decyls, undecyls, and dodecyls, for example), other silicon-organic compounds such as hexamethyldisilazane, fluoro-silicic acid salts such as ammonium hexafluorosilicate [$(NH_4)_2SiF_6$], quaternary ammonium silicate solutions (e.g., $(NR_4)n$, $(SiO_2)$, where R=H, or alkyls such as listed above, and when n=0.1-2, for example), aqueous sodium and potassium silicate solutions ($Na_2SiO_3$, $K_2SiO_3$, and $MSiO_3$ wherein M is Na or K in varying amounts in ratio to Si), silicic acid ($Si(OH)_4$) generated by ion exchange of any of the cationic forms of silica listed herein using an acidic ion-exchange resin (e.g., ion-exchange of the alkali-silicate solutions or quaternary ammonium silicate solutions).

**[0037]** The term "low molecular weight form" of silica refers to a silica species having a molecular weight (MW) of less than about 100,000. The term "small nanoparticle form" refers to silica particles having diameters < 5 nm.

**[0038]** The emphasis on thermal/hydrothermal stability improvement for vanadia-based catalysts is relatively new since this segment of the mobile emission control market is just developing. It was only after extensive characterization by the inventor of traditional catalysts that it was recognized that optimization of the vanadia-based catalysts required that (1) overall silica level needed to be minimized, and that (2) the soluble, low molecular weight and/or small nanoparticle form, forms of silica were most effective towards providing the requisite stability and activity.

**[0039]** The catalytic support materials of the present invention have

exceptional retention of the anatase phase of titania and surface area after severe thermal and/or hydrothermal treatments, even in the presence of vanadia. The compositions and methods of manufacture of the invention use low molecular weight and/or small nanoparticle forms of silica to obtain an exceptional ultrafine anatase titania phase and surface area stability, while the finished vanadia catalyst demonstrates equal or improved catalytic activity for vanadia-based selective catalytic reduction of NOx after accelerated aging. Such compositions and methods have been previously unknown in the art.

**[0040]** Two key aspects of the present invention that differentiate it over the prior art involve the nature of the amorphous silica and the manner in which it is incorporated into the titania.

**[0041]** With regard to the nature of the amorphous silica, it is first necessary to make the distinction between particulate forms of amorphous silica, and solution- or gas-phase forms that consist of very low molecular weight amorphous silicate monomers or clusters that are not considered to be in particulate form or comprise very small nanoparticles. The suitable forms of silica for the present invention are described herein and referred to as low molecular weight and/or small (< 5 nm) nanoparticle silica. Two references that describe the types of amorphous silica are "Ullmann's Encyclopedia of Industrial Chemistry, Fifth ed., Vol A23, pp. 583-660, (1993) and "The Chemistry of Silica", R. K. Iler, 1979. For example, one form of particulate amorphous silica is colloidal silica or silica sol. This type of silica consists of suspensions of dense, discrete amorphous silica particles that have diameters in the size range between about 5 nm and 100 nm. In this size range, the particles typically scatter visible light and thus form turbid to opaque suspensions. These particles can also typically be analyzed by visible light scattering methods using commonly available commercial instruments. As will be seen from the examples below, without further modification, colloidal silica in particulate form (>5 nm) is not a suitable form of silica for the present invention. One reason that this form of silica is not desirable (without subsequent modification) according to the present invention is that most of the mass of the silica in the particle is in the interior, and is not available at the surface to interact with the substrate titania. Thus, according to Iler (op cit., p. 8), an amorphous

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, for the purposes of the present invention, it is 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 inention 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 of the present invention 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

atoms near the surface and available for interaction with the titania. Of course, these secondary particles are easily analyzed using the visible light scattering methods, and when maintained in suspension, the particles are quite opaque. Particulate silica in any of these forms, without subsequent modification, is also not suitable for the present invention.

**[0046]** One class of silica precursor that is suitable for the present invention is the highly alkaline solutions, referred to as the water soluble silicates. These are described in Iler (op cit., Chapter 2). These solutions are typically transparent since the silica particles, if present, are generally too small to scatter visible light. However, depending on the silica concentration and alkalinity, small particles of silica can form in these solutions. Iler (op cit., p.133) estimates that for a $SiO_2$: $Na_2O$ molar ratio of 3.1, the average number of $SiO_2$ units per particle in dilute solutions is about 900, which is less than the 1500 silicate units in the 5 nm particle described above. Such a silicate precursor, even though it may contain some nanoparticles above about 5 nm, is suitable for the present invention since most of the mass of the silica is in the form of smaller, low molecular weight species. The alkali silicates are not the most preferable form for the present invention, however, because residual alkali ions such as Na are extremely effective catalyst poisons for vanadia-based SCR catalysts.

**[0047]** Recently, the nature of amorphous silica nanoparticles in alkaline solutions has been examined in more detail by Fedeyko, et. al., ("Langmuir", 2005, 21, 5197-5206). These authors used a variety of techniques, including small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS). These methods are able to detect the presence of nanoparticles down to about 2 to 3 nm in size. The authors showed that in dilute solution, when $[OH]/[SiO_2]$ is less than about 1, the silica forms small nanoparticles, while for $[OH]/[SiO_2]$ greater than 1, the silica is present as monomers and oligomers that are too small to be detected in the scattering experiments. It is the latter type of amorphous silica species, mostly too small to be easily detected by visible light and x-ray scattering methods, that are referred to as low molecular weight and/or small nanoparticle amorphous silica in the present invention, and these are the preferred forms of silica for the present invention.

**[0048]** One useful means of characterizing the silica monomers and

oligomers in solution is $^{29}Si$ nuclear magnetic resonance (see, for example, Chapter 3 in the book "High Resolution Solid-State NMR of Silicates and Zeolites" by G. Engelhardt and D. Michel, 1987). The method can provide information on the usual tetrahedral coordination environment around Si, and in particular, whether or not the Si contains one or more Si next nearest neighbors (linked by bridging oxygens). Notation that is commonly used to describe this coordination is as follows: $Q^0$ refers to a central Si with no next nearest Si neighbors, i.e., $Si(OH)_4$; $Q^1$ refers to a central Si with one next nearest Si neighbors, i.e., $Si(OH)_3(OSi)_1$; $Q^2$ refers to a central Si with two next nearest Si neighbors, i.e., $Si(OH)_2(OSi)_2$; $Q^3$ refers to a central Si with three next nearest Si neighbors, i.e., $Si(OH)_1(OSi)_3$; and $Q^4$ refers to a central Si with four next nearest Si neighbors, i.e., $Si(OSi)_4$.

**[0049]** Without being bound by theory, it is believed that in order to be used directly (without subsequent treatment to change the form of silica) it is desired to use silicate solutions that consist predominantly of $Q^0$ to $Q^3$ oligomers. On the other hand solutions of silicate oligomers that consist almost entirely of $Q^4$ species are not desired for the present invention. Conceptually, it is reasoned that for the latter types of silicate oligomers, much of the silica is completely surrounded by other silicate species and hence is unavailable for reaction with the titania surface, where it is most needed to stabilize the anatase.

**[0050]** One form of silica that is suitable for use in the present invention is the commercially available alkaline solution tetramethylammonium silicate. Insight can be gained into the nature of this solution based on earlier research. Engelhardt and Michel (op cit. p. 92) describe the $^{29}Si$ nuclear magnetic resonance study of a 1M solution of $SiO_2$ (approximately 6 wt%) with TMA/Si = 1.0, which is roughly equivalent to a TMAOH concentration of 9 wt%. In this solution, the silica is primarily in the form of a cubic octamer that contains 8 silicon atoms, and these have $Q^3$ coordination. This small species represents about 90% of the mass of the silica. The actual TMA-silicate solution used in the examples of the present invention has a somewhat higher concentration of silica (9 wt%) and lower concentration of TMAOH (7 wt%) and so the distribution of silicate species is somewhat different than the above literature report as shown in Table 6, below.

**[0051]** Another form of silica that is suitable for the present invention is "silicic acid". This type of silica is described in Iler (op cit., Chapter 3). A more detailed characterization of silicic acid is accomplished using the $^{29}Si$ nuclear magnetic resonance characterization, as described in G. Engelhardt and D. Michel (op cit. p. 100). This form of silica can be made by acidification of alkali silicate solutions, for example by ion-exchange using acidic ion exchange resins.

**[0052]** Fractional Monolayer Concept.

**[0053]** It is of interest to show that the compositions and methods of the present invention are different from prior art examples, and one means of doing so involves the notion of fractional monolayer coverage of the substrate surface with an added oxide. In the definitions below, the subscript x denotes the added oxide of interest, e.g., silica.

**[0054]** $C_x$ = Surface area-basis amount of added oxide for perfect monolayer coverage, $g/m^2$;

SA = Surface area of mixed oxide;

$M_x$ = Mass basis amount of added oxide for perfect monolayer coverage; g/g mixed oxide;

$L_x$ = Actual loading of added oxide on mixed oxide, g/g;

$FM_x$ = Fractional monolayer of added oxide on aged mixed oxide;

TFM =Total fractional monolayer on aged mixed oxide.

$M_x = C_x * SA$ (Eqn 1).

$FM_x = L_x/M_x$ (Eqn. 2)

$TFM = Sum(FM_x)$ (Eqn. 3)

**[0055]** First, it was necessary to establish a best estimate for the monolayer coverage of perfectly well-dispersed added oxides on the substrate titania or similar oxides, $C_x$. For vanadia, the literature value for monolayer coverage of the supported oxide is 7-8 V atoms/$nm^2$, which corresponds to 1,100 micrograms $V_2O_5$ /$m^2$. (see I. E. Wachs, et al., 2003). For tungsta, the literature value of 4.5 W atoms/$nm^2$ was used (I. E. Wachs, 2006), which corresponds to 1700 microgram $WO_3/m^2$. For silica, the literature value of 600 microgram $SiO_2/m^2$ was obtained (Iler, p. 36, op cit.). Thus, as an example, a mixed oxide consisting of 10 wt% $SiO_2$ (0.10 g/g), 9 wt% $WO_3$ (0.09 g/g) and 2 wt% $V_2O_5$ (0.02 g/g) with the balance $TiO_2$, has a measured $N_2$ BET surface area of 250 $m^2/g$. The TFM for this

material is TFM = (1/250)* ((0.10/600E-6) + (0.09/1700E-6) + (0.02/1100E-6)) = 0.95. This number indicates that were the added $SiO_2$, $WO_3$ and $V_2O_5$ oxides perfectly well dispersed on the titania surface, the surface coverage of the final, mixed oxide would be 0.95 monolayers thick with the added oxides. With respect to silica alone, the fractional monolayer coverage would be 0.67, or two-thirds of the surface would be covered with an ideally dispersed silica coating. The compositions of the present invention, when freshly prepared (i.e., after the addition of the added oxides but before aging or sintering) typically have surface areas greater than about 100 $m^2/g$ and a total amount of added oxides of 15 wt% or less, and so the fractional monolayer coverage is about 1.0 or less, and the fractional monolayer coverage specifically for silica is about 0.80 or less.

**[0056]** Methods of silica incorporation for the present invention.

**[0057]** The surface coating of titania using alkali silicates or silicic acid such as described above has been practiced industrially for many years in the paints and coatings industry. See, for example, the review chapters 52 and 53 in the "Colloidal Silica, Fundamentals and Applications", Surfactant Science Series Vol. 131, H. E. Bergna, W. O. Roberts, eds. (2006). As described in Ch. 52 of Bergna and Roberts, one approach to coating the titania surface with silica involves exposing the substrate titania particles to silica under alkaline conditions with a concentration of silica that is below the solubility limit for amorphous silica. As described in Ch. 53 of Bergna and Roberts, another method involves exposing the substrate titania surface to monosilicic acid at low pH at a silica concentration that is again very low and below the solubility limit. While the methods for silica incorporation in the above references represent suitable means of incorporating silica according to the present invention, there are several important differences. One difference is that for the prior art, the phase of titania that is used as the substrate is rutile (because of its higher light scattering power than anatase), and there is no suggestion of the ability of silica addition via those methods for the prevention of anatase phase conversion to rutile. A second important difference is that the substrate titania particles of the paints and coatings prior art, regardless of whether they are anatase or rutile, are relatively low surface area substrates, with $N_2$ BET surface areas of the substrate surface typically being less than

about 15 $m^2/g$. Third, a key difference is in the surface coverage of the added oxide such as silica. With the above definition of fractional monolayer coverage, the compositions of the present invention, if they were prepared on a low surface area support (15 $m^2/g$) would have total fractional monolayer of about 5 or greater, and the fractional monolayer coverage specifically for silica would be about ≥3. Thus, in the prior art, the silica coating is present over the entire titania particle, and with a thickness that exceeds the thickness of a monolayer. Indeed, the silica coating is present so as to completely inactivate the photo-catalytic activity of the titania surface. Finally, in a preferred embodiment of the present invention, the titania is coated with silica under conditions where the added silica is well above the solubility limit of a few hundred ppm. As will be seen below, in the present invention the silica, when it is deposited initially, does not completely cover the titania surface, so that the desirable catalytic functionality of the titania surface for the SCR reaction is still available. Hence, the goal of the present invention of maximizing the catalytic activity of the surface can then be met, while preserving the stability of the support.

**[0058]** There is one more reason why particulate silicas are not the preferred forms of silica for the present invention, including forms of particulate silica with internal porosity and hence high pore volume. It is well know from the literature (e.g., Wachs et al., *J. Cat.* 161, 211-221 (1996)) that silica, by itself, is not a good support for vanadia SCR catalysts, while titania and tungsta-doped titania are good supports. Hence, for the present invention, it is desirable to minimize the amount of silica surface area that is available to adversely interact with vanadia, while maximizing the amount of $TiO_2/WO_3$ surface area, so as to make the most active catalyst. Thus, only enough silica is used to stabilize the titania, and it is used in a form (molecularly dispersed on the titania surface) that has minimal adverse impact on the vanadia catalyst.

**[0059]** Finally, another approach to make the materials of the present invention, wherein the particulate forms of silica described above can be used, is now described. It is well known that particulate amorphous silica is soluble to an extent that depends on solution pH and temperature, see for example Iler, (op cit., p. 42). Above about pH 9 and for temperatures

higher than ambient temperature, amorphous silica will appreciably dissolve. This dissolved silica can then be precipitated again, for example onto a titania surface, by subsequently lowering the temperature and/or pH to a region that has lower silica solubility. In this manner, particulate silicas that are finely mixed with anatase titania can be dissolved and redistributed in a well-dispersed manner onto the titania surface via the hydrothermal treatment. However, such a post-treatment is not a preferred method of making the compositions of the present invention, since this step adds processing time and cost during the mixed oxide manufacture. It is most preferred to use a suitable silica precursor and treat the titania directly.

**[0060] EXAMPLES**

**[0061]** Titania Starting Material

**[0062]** In one embodiment of the present invention, a sulfated titania slurry (see Table 1) was used. Such a sulfated titania slurry can be obtained as an intermediate product in a production process for making titanium dioxide using the sulfuric acid process, for example as produced by the MIC production facility in Thann, France. Such a slurry comprises about 27% of a high surface area, hydrous anatase titania, $TiO_2$. The $TiO_2$ has primary crystallite particles having sizes of less than 5 nanometers, and corresponding $N_2$ BET surface areas in excess of 250 $m^2/g$. The slurry has a viscosity of 0.5-3 poises, a density of 1275 $kg/m^3$, and a low pH of around 1.5 - 2.0, which results from the fact that the slurry contains about 6.6 wt% $SO_3$. However, the present invention is not restricted to use of this slurry. Any composition comprising hydrous anatase titania could be used herein. Indeed, it is not necessary to use a sulfated titania slurry as the starting material. A dried low-sulfate anatase titania precursor could be used instead.

**[0089]** Example 6: Silica Surface Stabilization

**[0090]** As noted elsewhere herein, the present invention is directed to providing a very stable ultrafine titania using a minimal amount of silica additive. As noted above, particulate silicas (e.g., colloidal, fumed, and precipitated) are not ideal sources of silica for use in titania-supported vanadium catalysts, because much of the silica is not available to interact with the titania surface. A goal of the present invention was to find another form of silica that could be used to more effectively stabilize the surface of the titania, but that would have a minimal adverse impact on the catalytic activity of vanadia supported on the surface of the titania.

**[0091]** The use of silica in low molecular weight and/or small nanoparticle form was considered, rather than in the particulate form which is present in the conventional amorphous silicas described above. The lowest molecular weight form of silica in aqueous solution is silicic acid, $Si(OH)_4$. However, this chemical entity has a very low solubility in water, and therefore is restricted to concentrations of a few hundred ppm. (Discussions of the aqueous chemistry of silica in water, are found for example, in Iler, (op cit.) and Brinker, C. J and Scherer, G. W, 1990, Chapter 3).

**[0092]** In view of the low solubility of $Si(OH)_4$, we turned to experimentation with tetra(alkyl)ammonium silicate solutions (including, but not limited to, tetramethylammonium, TMA). These reagents contain silica in low molecular weight forms (see Engelhardt and Michel, op cit.). Furthermore, the silica in these solutions is present at fairly high concentrations (e.g., 9 wt% $SiO_2$). Thus, we considered whether or not the molecular entities in these solutions may be small enough to react selectively with the titania surface, while not providing separate area for vanadia to bond which would diminish its catalytic activity.

**[0093]** $^{29}$Si NMR spectroscopy of a liquid sample of soluble silicate.

**[0094]** In order to determine the nature of the silicate species in commercially available TMA silicate solution, the commercial source of TMA silicate used in these examples (Alfa TMA-silicate, 9% $SiO_2$) was evaluated using $^{29}$Si NMR spectroscopy on a 400 MHz instrument by Spectral Data Services, Inc. Shown in Table 6 are the results.

What is claimed is:

1. A catalyst support material, comprising:

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.

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

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 2 comprising ≥ 85% dry weight of $TiO_2$, 3% - 9% of $SiO_2$, and 3% - 9% dry weight of $WO_3$.

5. The catalyst support material of claim 1 or 2, wherein the $SiO_2$ is present at a fractional monolayer value of less than 1.0 before the catalyst support material is sintered.

6. The catalyst support material of claim 1 or 2, wherein the small nanoparticle form of the $SiO_2$ comprises a diameter of < 5 nm.

7. The catalytic support material of any one of claims 1-4, wherein the low molecular weight form of the $SiO_2$ comprises a molecular weight of < 100,000.

8. The catalytic support material of claim 1 or 2, wherein the $SiO_2$ comprises silicon atoms which are substantially in the $Q^3$, $Q^2$, $Q^1$ and $Q^0$ coordination environments.

9. The catalytic support material of claim 1 or 2, wherein the $SiO_2$ comprises patches which are substantially ≤5 nm deep after redistribution as seen by scanning electron microscopy or by transmission electron microscopy.

10. The catalytic support material of claim 1 or 2, wherein the $TiO_2$ was not prepared in the presence of urea.

11. A vanadia catalyst, comprising :

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

12. The vanadia catalyst of claim 11 comprising 0.5% to 5% dry weight of $V_2O_5$.

13. The vanadia catalyst of claim 11 or 12, wherein the $V_2O_5$ thereof is present at a fractional monolayer value of less than 1.0 before sintering.

14. The vanadia catalyst of claim 11 or 12, which has been sintered at ≥ $650^0$C.

15. A diesel emission catalytic device comprising the vanadia catalyst of claim 11 or 12.

16. A diesel emission control system, comprising:

the diesel emission catalytic device of claim 15; and

a diesel particulate filter, and wherein the diesel emission catalytic device is positioned upstream

of or downstream of the diesel particulate filter.

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

exposing engine emissions comprising NOx to the vanadia catalyst of claim 11 or 12 with an added reductant to produce $N_2$ and $H_2O$.

18. The method of claim 17 wherein the reductant is $NH_3$ and/or urea.

19. The method of claim 17 or 18, wherein the vanadia catalyst comprises 0.5%- 3% dry weight of $V_2O_5$.

20. The method of claim 17 or 18, wherein the engine emissions are passed through a diesel particulate filter before or after being exposed to the vanadia catalyst.

21. 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 $SiO_2$ substantially in a low molecular weight and/or $SiO_2$ comprising small nanoparticles 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.

22. The method of claim 21 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.

23. The method of claim 21 or 22, wherein the $TiO_2$ of the slurry comprise preformed titanium hydroxide, titanium oxy-hydroxide or titanium dioxide particles.

24. The method of claim 21 or 22, wherein the $TiO_2$ of the slurry is not produced in the presence of urea.

25. The method of claim 21 or 22, wherein the small nanoparticle form of the $SiO_2$ of the silica precursor solution substantially comprises a diameter of < 5 nm.

26. The method of claim 21 or 22, wherein the low molecular weight form of the $SiO_2$ of the silica precursor solution substantially comprises a MW of < 100,000.

27. The method of claim 21 or 22, wherein the $SiO_2$ of the silica precursor solution comprises silicon atoms which are substantially in the $Q^3$, $Q^2$, $Q^1$ and $Q^0$ coordination environments.

28. The method of claim 21 or 22, wherein the silica precursor solution comprises a tetra(alkyl)ammonium silicate solution or silicic acid.

29. The method of claim 21 or 22, wherein the $SiO_2$ substantially comprises patches which are $\leq$5 nm in depth after redistribution as seen by scanning electron microscopy or by transmission electron microscopy.

30. The method of claim 21 or 22, comprising combining the $TiO_2$-$WO_3$-$SiO_2$ mixture with $V_2O_5$ to form a vanadia catalyst.

31. The method of claim 30 wherein the vanadia catalyst comprises 0.5%- 3% dry weight of $V_2O_5$.

32. The method of claim 30 or 31, wherein the $V_2O_5$ of the vanadia catalyst is present at a fractional monolayer value of less than 1.0 before sintering.

33. The method of claim 30 or 31, comprising the additional step of sintering the vanadia catalyst at $\geq$650°C.

34. A method of producing a silica-stabilized titania catalyst support material, 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 reprecipitated on the $TiO_2$ particles to form the silica-stabilized titania catalyst support material.

35. The method of claim 34 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.

36. The method of claim 35 further comprising washing and sintering the silica-stabilized titania tungsten catalyst support material.

37. The method of claim 35 or 36, 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.

38. The method of claim 34, 35 or 36, wherein the $TiO_2$ particles of the $TiO_2$ slurry comprise preformed titanium hydroxide, titanium oxy-hydroxide or titanium dioxide particles.

39. The method of claim 34, 35 or 36, wherein the $TiO_2$ particles of the $TiO_2$ slurry are not produced in the presence of urea.

40. The method of claim 34, 35 or 36, wherein the $SiO_2$ of the $TiO_2$-$SiO_2$ mixture, after dissolving, comprises silicon atoms which are substantially in the $Q^3$, $Q^2$, $Q^1$ and $Q^0$ coordination environments.

41. The method of claim 34, 35 or 36, wherein the $SiO_2$ on the $TiO_2$ particles substantially comprises patches which are $\leq$5 nm in depth after redistribution of the $SiO_2$ as seen by scanning electron microscopy or by transmission electron microscopy.

42. The method of claim 35 or 36, comprising combining the $TiO_2$-$WO_3$-$SiO_2$ mixture with $V_2O_5$ to form a vanadia catalyst.

43. The method of claim 42, wherein the vanadia catalyst comprises 0.5%- 3% dry weight of $V_2O_5$.

44. The method of claim 42, wherein the $V_2O_5$ of the vanadia catalyst is present at a fractional monolayer value of less than 1.0 before sintering.

45. The method of claim 42, comprising the additional step of sintering the vanadia catalyst at $\geq$650°C.

46. Anatase titania particles, comprising:

greater than or equal to 85 percent by dry weight of $TiO_2$; and greater than 0 percent and less than or equal to 10 percent by dry weight of silica, wherein the (i) silica is substantially in a form selected from the group consisting of low molecular weight oligomers, nanoparticles, and combinations thereof, and (ii) at least 50% of the silicon atoms of the silica are in $Q^3$, $Q^2$, $Q^1$ and $Q^0$ coordination environments.

47. The anatase titania particles of claim 46, further comprising from about 3% to about 10% $WO_3$ by weight of the anatase titania particles.

48. The anatase titania particles of claim 46 or 47, having a BET surface area of at least 80 $m^2/g$.

49. The anatase titania particles of claim 46 or 47, comprising greater than or equal to 85 percent by dry weight of anatase $TiO_2$, from about 3 percent to about 9 percent by dry weight of silica, and from about 3 percent to about 9 percent by dry weight of $WO_3$.

50. The anatase titania particles of claim 46 or 47, wherein the silica is present at a fractional monolayer value of less than or about 1.0.

51. The anatase titania particles of claim 46 or 47, wherein the silica comprises patches having thicknesses of about 1 nm to about 3 nm as determined by at least one of scanning electron

microscopy and by transmission electron microscopy.

52. A catalyst support material comprising the anatase titania particles of claim 46 or 47.

53. Anatase titania particles, comprising: greater than or equal to 85 percent by dry weight of $TiO_2$ from about 3 percent to about 9 percent by dry weight of silica, and from about 3 percent to about 9 percent by dry weight of $WO_3$, wherein (i) the silica is substantially in a form selected from the group consisting of low molecular weight oligomers, nanoparticles and combinations thereof and (ii) at least 50% of the silicon atoms of the silica are in the $Q^3$, $Q^2$, $Q^1$ and $Q^0$ coordination environments.

54. The anatase titania particles of claim 53, having a BET surface area of at least 80 $m^2/g$.

55. The anatase titania particles of claim 53 or 54, wherein the silica is present at a fractional monolayer value of less than or about 1.0.

56. The anatase titania particles of claim 53 or 54, wherein the silica comprises patches having thicknesses of about 1 nm to about 3 nm as determined by at least one of scanning electron microscopy and transmission electron microscopy.

57. A catalyst support material comprising the anatase titania particles of claim 53 or 54.

58. The catalyst support material of claim 57, further comprising $V_2O_5$ disposed thereon.

59. The catalyst support material of claim 58 comprising 0.5% to 5% dry weight of $V_2O_5$.

60. The catalyst support material of claim 58 or 59, wherein the $V_2O_5$ thereof is present at a fractional monolayer value of less than 1.0 before sintering.

61. The catalyst support material of claim 58 or 59, which has been sintered at >650° C.

62. A diesel emission catalytic device comprising the vanadia catalyst of claim 58 or 59.

63. A diesel emission control system, comprising: the diesel emission catalytic device of claim 17; and a diesel particulate filter, and wherein the diesel emission catalytic device is positioned upstream of or downstream of the diesel particulate filter.

64. A method of catalyzing the conversion of nitrogen oxides to $N_2$ gas, comprising: exposing engine emissions comprising NOx to the vanadia catalyst of claim 58 or 59 with an added reductant to produce $N_2$ and $H_2O$.

65. The method of claim 64, wherein the reductant is $NH_3$ and/or urea.

66. The method of claim 64 or 65, wherein the vanadia catalyst comprises 0.5%-3% dry weight

of $V_2O_5$.

67. The method of claim 64 or 65, wherein the engine emissions are passed through a diesel particulate filter before or after being exposed to the vanadia catalyst.

68. Anatase titania particles, comprising: a nominal composition of 81 percent by dry weight of $TiO_2$, 10 percent by dry weight of silica, and 9 percent by dry weight of $WO_3$, wherein (i) the silica is substantially in a form selected from the group consisting of low molecular weight oligomers, nanoparticles and combinations thereof and (ii) at least 50% of the silicon atoms of the silica are in the $Q^3$, $Q^2$, $Q^1$ and $Q^0$ coordination environments.

69. The anatase titania particles of claim 68, having a BET surface area of at least 80 $m^2/g$.

70. The anatase titania particles of claim 68 or 69, wherein the silica is present at a fractional monolayer value of less than or about 1.0.

71. The anatase titania particles of claim 68 or 69, wherein the silica comprises patches having thicknesses of about 1 nm to about 3 nm as determined by at least one of scanning electron microscopy and transmission electron microscopy.

72. A catalyst support material comprising the anatase titania particles of claim 68 or 69.

**[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 $SiO_2$ may be present at a fractional monolayer value of less than 1.0 before the catalyst support material is sintered. The small nanoparticle form of the $SiO_2$ may comprise a diameter of <5nm. The low molecular weight form of the $SiO_2$ may comprise 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

comprising a silica-stabilized titania catalyst support material as described herein which comprises $V_2O_5$ disposed thereon. The vanadia catalyst may comprise, for example, 0.5% to 5% dry weight Of $V_2O_5$ (or more preferably 1.0 to 3%). The $V_2O_5$ may be present at a fractional monolayer value of less than 1.0 before sintering. The vanadia catalyst may be sintered at ≥ $650^0$C for example. In another aspect, a diesel emission catalytic device comprising the vanadia catalyst is described herein. In another aspect a diesel emission control system which comprises the diesel emission catalytic device described above and a diesel particulate filter, and wherein the diesel emission catalytic device is positioned upstream of or downstream of the diesel particulate filter.

**[0014]** In another one of its aspects, a method of catalyzing the conversion of nitrogen oxides to $N_2$ gas, comprising exposing engine emissions comprising NOx to the vanadia catalyst is described herein with an added reductant to produce $N_2$ and $H_2O$. The reductant may be for example $NH_3$and/or urea. In the method the vanadia catalyst may comprise 0.5%-5% (or more preferably 1.0% to 3%) dry weight of $V_2O_5$, for example. The engine emissions may be passed through a diesel particulate filter before or after being exposed to the vanadia catalyst.

**[0015]** In another of its aspects, 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 $SiO_2$ substantially in a low molecular weight form and/or $SiO_2$ comprising small nanoparticles 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 then washing and sintering the $TiO_2$-$WO_3$.$SiO_2$ mixture to form a silicastabilized titania support material is described. In the method the silica-stabilized titania 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 $TiO_2$ of the slurry may comprise, for example, preformed titanium hydroxide, titanium oxyhydroxide or titanium dioxide particles. Optionally, the $TiO_2$ of the slurry is

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 $Q^0$coordination 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 a 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

substantially (e.g., > 50%) in the $Q^3$, $Q^2$, $Q^1$and $Q^0$ coordination environments. The $SiO_2$ on the $TiO_2$ particles of the method may substantially comprise patches which are ≤5 nm in depth after redistribution of the $SiO_2$ 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. In the method, the vanadia catalyst may comprise, for example, 0.5%- 3% dry weight of $V_2O_5$. The $V_2O_5$ of the vanadia catalyst may be present at a fractional monolayer value of less than 1.0 before sintering, and the vanadia catalyst may be sintered at ≥650°C.

**[0017]** Other aspects will become evident upon consideration of the description below.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0018]** Figure 1 is a graph showing the effect of calcination temperature on surface area of vanadia catalyst.

**[0019]** Figure 2 is a graph showing the effect of calcination temperature on the percentage of anatase phase of titania in vanadia catalysts.

**[0020]** Figure 3 is a graph showing the effect of calcination temperature on DeNox activity of 1% vanadia catalysts.

**[0021]** Figure 4 is a graph showing the effect of calcination temperature on DeNOx conversion of 3% vanadia catalysts.

**[0022]** Figure 5 is a graph showing the effect of temperature on DeNOx activity of various vanadia catalysts.

**[0023]** Figure 6 is a graph showing the effect of temperature on surface area of a catalyst support as described herein versus a conventional catalyst support.

**[0024]** Figure 7 is a transmission electron micrograph (TEM) of a silica-tungsta-titania catalyst of Example 6 showing two-dimensional patches of silica <2 nm in depth on the titania surface.

**[0025]** Figure 8 is a scanning electron micrograph of a vanadia-titania catalyst of Example 10 showing ~20 nm colloidal silica particles disposed thereon.

**[0026]** Figure 9 is a transmission electron micrograph (TEM) of a catalyst showing ~20 nm colloidal silica particles on the outer surface of the

vanadia-titania catalyst of Example 10.

**[0027]** Figure 10 is a transmission electron micrograph (TEM) of the catalytic particles of Example 11, showing anatase crystals with a patchy, two-dimensional silica layer on the outer crystal surface. In this image, no silica particles are observable.

**[0028]** Figure 11 is a transmission electron micrograph (TEM) of the catalytic particles of Example 11, showing anatase crystals with a patchy, two-dimensional silica layer on the outer crystal surface. In this image, one remnant silica particle that is <5 nm in diameter can be seen.

**[0029]** Figure 12 is a transmission electron micrograph (TEM) of the catalytic particles of Example 12, showing small, two-dimensional patches of silica on the anatase crystallites.

**[0030]** Figure 13 is a transmission electron micrograph of silica patches present on the surface of the catalytic particles of anatase titania of Example 13.

**[0031]** Figure 14 is a transmission electron micrograph of silica patches present on the surface of the catalytic particles of anatase titania of Example 13.

**[0032]** Figure 15 is a transmission electron micrograph (TEM) of the catalyst support before vanadia addition and sintering. The image shows the lattice fringes associated with anatase titania; the silica is present as 1- 3 nm patches on the titania surface (Example 14).

**[0033]** Figure 16 is a transmission electron micrograph (TEM) of the vanadia catalyst that shows large (>20 nm) three dimensional silica nodules (see arrows) that are not well dispersed on the titania surface (e.g., Example 15).

**[0034]** Figure 17 is another transmission electron micrograph (TEM) of the vanadia catalyst that shows large (>20 nm) three dimensional silica nodules (see arrows) that are not well dispersed on the titania surface (e.g., Example 15).

**[0035]** Figure 18 is a graph showing the effect of various calcination (activation) temperatures on the deNOx catalytic activities of forms of titania-supported vanadium catalysts.

## DETAILED DESCRIPTION

**[0036]** Production of a

stable, high surface area titania support material in anatase crystal form, primarily to be used as a support for vanadia ($V_2O_5$) in diesel emission control catalyst applications. The stabilization involves treatment of the titania with silica in a low molecular weight form and/or small nanoparticle form, such as a soluble precursor tetra(alkyl)ammonium silicate (i.e., tetramethylammonium silicate) or tetraethylorthosilicate (TEOS). Other examples of low molecular weight silica precursors which may be used include, but are not limited to aqueous solutions of silicon halides (i.e., anhydrous $SiX_4$, where X= F, Cl, Br, or I), silicon alkoxides (i.e., $Si(OR)_4$, where R=methyl, ethyl, isopropyl, propyl, butyl, iso-butyl, sec-butyl, tert-butyl, pentyls, hexyls, octyls, nonyls, decyls, undecyls, and dodecyls, for example), other silicon-organic compounds such as hexamethyldisilazane, fluoro-silicic acid salts such as ammonium hexafluorosilicate [$(NH_4)_2SiF_6$], quaternary ammonium silicate solutions (e.g., $(NR_4)n$, $(SiO_2)$, where R=H, or alkyls such as listed above, and when n = 0.1-2, for example), aqueous sodium and potassium silicate solutions ($Na_2SiO_3$, $K_2SiO_3$, and $MSiO_3$ wherein M is Na or K in varying amounts in ratio to Si), silicic acid ($Si(OH)_4$) generated by ion exchange of any of the cationic forms of silica listed herein using an acidic ion-exchange resin (e.g., ion-exchange of the alkali-silicate solutions or quaternary ammonium silicate solutions).

**[0037]** The term "low molecular weight form" of silica refers to a silica species having a molecular weight (MW) of less than about 100,000. The term "small nanoparticle form" refers to silica particles having diameters < 5 nm.

**[0038]** The emphasis on thermal/hydrothermal stability improvement for vanadia-based catalysts is relatively new since this segment of the mobile emission control market is just developing. It was only after extensive characterization by the inventor of traditional catalysts that it was recognized that optimization of the vanadia-based catalysts required that (1) overall silica level needed to be minimized, and that (2) the soluble, low molecular weight and/or small nanoparticle form, forms of silica were most effective towards providing the requisite stability and activity.

**[0039]** The catalytic support materials as described herein have

exceptional retention of the anatase phase of titania and surface area after severe thermal and/or hydrothermal treatments, even in the presence of vanadia. The compositions and methods of manufacture use low molecular weight and/or small nanoparticle forms of silica to obtain an exceptional ultrafine anatase titania phase and surface area stability, while the finished vanadia catalyst demonstrates equal or improved catalytic activity for vanadia-based selective catalytic reduction of NOx after accelerated aging. Such compositions and methods have been previously unknown in the art.

**[0040]** Two aspects that may differentiate it over the prior art involve the nature of the amorphous silica and the manner in which it is incorporated into the titania.

**[0041]** With regard to the nature of the amorphous silica, it is first necessary to make the distinction between particulate forms of amorphous silica, and solution- or gas-phase forms that consist of very low molecular weight amorphous silicate monomers or clusters that are not considered to be in particulate form or comprise very small nanoparticles. The suitable forms of silica are described herein and referred to as low molecular weight and/or small (< 5 nm) nanoparticle silica. Two references that describe the types of amorphous silica are "Ullmann's Encyclopedia of Industrial Chemistry, Fifth ed., Vol A23, pp. 583-660, (1993) and "The Chemistry of Silica", R. K. ller, 1979. For example, one form of particulate amorphous silica is colloidal silica or silica sol. This type of silica consists of suspensions of dense, discrete amorphous silica particles that have diameters in the size range between about 5 nm and 100 nm. In this size range, the particles typically scatter visible light and thus form turbid to opaque suspensions. These particles can also typically be analyzed by visible light scattering methods using commonly available commercial instruments. As will be seen from the examples below, without further modification, colloidal silica in particulate form (>5 nm) may not be a suitable form of silica. One reason that this form of silica may not be desirable (without subsequent modification) is that most of the mass of the silica in the particle is in the interior, and is not available at the surface to interact with the substrate titania. Thus, according to ller (op cit., p. 8), an amorphous

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 inention 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

atoms near the surface and available for interaction with the titania. Of course, these secondary particles are easily analyzed using the visible light scattering methods, and when maintained in suspension, the particles are quite opaque. Particulate silica in any of these forms, without subsequent modification, may also not be suitable.

**[0046]** One class of silica precursor that may be suitable is the highly alkaline solutions, referred to as the water soluble silicates. These are described in Iler (op cit., Chapter 2). These solutions are typically transparent since the silica particles, if present, are generally too small to scatter visible light. However, depending on the silica concentration and alkalinity, small particles of silica can form in these solutions. Iler (op cit., p.133) estimates that for a $SiO_2$: $Na_2O$ molar ratio of 3.1, the average number of $SiO_2$units per particle in dilute solutions is about 900, which is less than the 1500 silicate units in the 5 nm particle described above. Such a silicate precursor, even though it may contain some nanoparticles above about 5 nm, may be suitable since most of the mass of the silica is in the form of smaller, low molecular weight species. The alkali silicates may not be the most preferable form, however, because residual alkali ions such as Na are extremely effective catalyst poisons for vanadia-based SCR catalysts.

**[0047]** Recently, the nature of amorphous silica nanoparticles in alkaline solutions has been examined in more detail by Fedeyko, et. al., ("Langmuir", 2005, 21, 5197-5206). These authors used a variety of techniques, including small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS). These methods are able to detect the presence of nanoparticles down to about 2 to 3 nm in size. The authors showed that in dilute solution, when [OH]/[$SiO_2$] is less than about 1, the silica forms small nanoparticles, while for [OH]/[$SiO_2$] greater than 1, the silica is present as monomers and oligomers that are too small to be detected in the scattering experiments. It is the latter type of amorphous silica species, mostly too small to be easily detected by visible light and x-ray scattering methods, that are referred to as low molecular weight and/or small nanoparticle amorphous silica, and these may be the preferred forms of silica.

**[0048]** One useful means of characterizing the silica monomers and

oligomers in solution is $^{29}Si$ nuclear magnetic resonance (see, for example, Chapter 3 in the book "High Resolution Solid-State NMR of Silicates and Zeolites" by G. Engelhardt and D. Michel, 1987). The method can provide information on the usual tetrahedral coordination environment around Si, and in particular, whether or not the Si contains one or more Si next nearest neighbors (linked by bridging oxygens). Notation that is commonly used to describe this coordination is as follows: $Q^0$ refers to a central Si with no next nearest Si neighbors, i.e., $Si(OH)_4$; $Q^1$ refers to a central Si with one next nearest Si neighbors, i.e., $Si(OH)_3(OSi)_1$; $Q^2$ refers to a central Si with two next nearest Si neighbors, i.e., $Si(OH)_2(OSi)_2$; $Q^3$ refers to a central Si with three next nearest Si neighbors, i.e., $Si(OH)_1(OSi)_3$; and $Q^4$ refers to a central Si with four next nearest Si neighbors, i.e., $Si(OSi)_4$.

**[0049]** Without being bound by theory, it is believed that in order to be used directly (without subsequent treatment to change the form of silica) it is desired to use silicate solutions that consist predominantly of $Q^0$to $Q^3$ oligomers. On the other hand solutions of silicate oligomers that consist almost entirely of $Q^4$ species may not be desired. Conceptually, it is reasoned that for the latter types of silicate oligomers, much of the silica is completely surrounded by other silicate species and hence is unavailable for reaction with the titania surface, where it is most needed to stabilize the anatase.

**[0050]** One form of silica that may be suitable for use is the commercially available alkaline solution tetramethylammonium silicate. Insight can be gained into the nature of this solution based on earlier research. Engelhardt and Michel (op cit. p. 92) describe the $^{29}Si$ nuclear magnetic resonance study of a 1M solution of $SiO_2$ (approximately 6 wt%) with TMA/Si = 1.0, which is roughly equivalent to a TMAOH concentration of 9 wt%. In this solution, the silica is primarily in the form of a cubic octamer that contains 8 silicon atoms, and these have $Q^3$ coordination. This small species represents about 90% of the mass of the silica. The actual TMA-silicate solution used in the examples has a somewhat higher concentration of silica (9 wt%) and lower concentration of TMAOH (7 wt%) and so the distribution of silicate species is somewhat different than the above literature report as shown in Table 6, below.

**[0051]** Another form of silica that may be suitable is "silicic acid". This type of silica is described in Iler (op cit., Chapter 3). A more detailed characterization of silicic acid is accomplished using the $^{29}Si$ nuclear magnetic resonance characterization, as described in G. Engelhardt and D. Michel (op cit. p. 100). This form of silica can be made by acidification of alkali silicate solutions, for example by ion-exchange using acidic ion exchange resins.

**[0052]** Fractional Monolayer Concept.

**[0053]** It is of interest to show that the compositions and methods as described herein are different from prior art examples, and one means of doing so involves the notion of fractional monolayer coverage of the substrate surface with an added oxide. In the definitions below, the subscript x denotes the added oxide of interest, e.g., silica.

**[0054]** $C_x$ = Surface area-basis amount of added oxide for perfect monolayer coverage, $g/m^2$;

SA = Surface area of mixed oxide;

$M_x$ = Mass basis amount of added oxide for perfect monolayer coverage; g/g mixed oxide;

$L_x$ = Actual loading of added oxide on mixed oxide, g/g;

$FM_x$ = Fractional monolayer of added oxide on aged mixed oxide;

TFM =Total fractional monolayer on aged mixed oxide.

$M_x = C_x * SA$ (Eqn 1).

$FM_x = L_x M_x$ , (Eqn. 2)

$TFM = Sum(FM_x)$ (Eqn. 3)

**[0055]** First, it was necessary to establish a best estimate for the monolayer coverage of perfectly well-dispersed added oxides on the substrate titania or similar oxides, $C_x$. For vanadia, the literature value for monolayer coverage of the supported oxide is 7-8 V atoms/$nm^2$, which corresponds to 1,100 micrograms $V_2O_5$ /$m^2$. (see I. E. Wachs, et al., 2003). For tungsta, the literature value of 4.5 W atoms/$nm^2$ was used (I. E. Wachs, 2006), which corresponds to 1700 microgram $WO_3/m^2$. For silica, the literature value of 600 microgram $SiO_2/m^2$ was obtained (Iler , p. 36, op cit.). Thus, as an example, a mixed oxide consisting of 10 wt% $SiO_2$ (0.10 g/g), 9 wt% $WO_3$ (0.09 g/g) and 2 wt% $V_2O_5$ (0.02 g/g) with the balance $TiO_2$, has a measured $N_2$ BET surface area of 250 $m^2/g$. The TFM for this

material is TFM = (1/250)* ((0.10/600E-6) + (0.09/1700E-6) + (0.02/1100E-6)) = 0.95. This number indicates that were the added $SiO_2$, $WO_3$ and $V_2O_5$ oxides perfectly well dispersed on the titania surface, the surface coverage of the final, mixed oxide would be 0.95 monolayers thick with the added oxides. With respect to silica alone, the fractional monolayer coverage would be 0.67, or two-thirds of the surface would be covered with an ideally dispersed silica coating. The compositions when freshly prepared (i.e., after the addition of the added oxides but before aging or sintering) typically have surface areas greater than about 100 $m^2/g$ and a total amount of added oxides of 15 wt% or less, and so the fractional monolayer coverage is about 1.0 or less, and the fractional monolayer coverage specifically for silica is about 0.80 or less.

**[0056]** Methods of silica incorporation.

**[0057]** The surface coating of titania using alkali silicates or silicic acid such as described above has been practiced industrially for many years in the paints and coatings industry. See, for example, the review chapters 52 and 53 in the "Colloidal Silica, Fundamentals and Applications", Surfactant Science Series Vol. 131, H. E. Bergna, W. O. Roberts, eds. (2006). As described in Ch. 52 of Bergna and Roberts, one approach to coating the titania surface with silica involves exposing the substrate titania particles to silica under alkaline conditions with a concentration of silica that is below the solubility limit for amorphous silica. As described in Ch. 53 of Bergna and Roberts, another method involves exposing the substrate titania surface to monosilicic acid at low pH at a silica concentration that is again very low and below the solubility limit. While the methods for silica incorporation in the above references represent suitable means of incorporating silica, there are several important differences. One difference is that for the prior art, the phase of titania that is used as the substrate is rutile (because of its higher light scattering power than anatase), and there is no suggestion of the ability of silica addition via those methods for the prevention of anatase phase conversion to rutile. A second important difference is that the substrate titania particles of the paints and coatings prior art, regardless of whether they are anatase or rutile, are relatively low surface area substrates, with $N_2$ BET surface areas of the substrate surface typically being less than

about 15 $m^2/g$. Third, a difference is in the surface coverage of the added oxide such as silica. With the above definition of fractional monolayer coverage, the compositions, if they were prepared on a low surface area support (15 $m^2/g$) would have total fractional monolayer of about 5 or greater, and the fractional monolayer coverage specifically for silica would be about ≥ 3. Thus, in the prior art, the silica coating is present over the entire titania particle, and with a thickness that exceeds the thickness of a monolayer. Indeed, the silica coating is present so as to completely inactivate the photo-catalytic activity of the titania surface. Finally, in a preferred embodiment, the titania is coated with silica under conditions where the added silica is well above the solubility limit of a few hundred ppm. As will be seen below, in the present invention the silica, when it is deposited initially, does not completely cover the titania surface, so that the desirable catalytic functionality of the titania surface for the SCR reaction is still available. Hence, maximizing the catalytic activity of the surface may then be met, while preserving the stability of the support.

**[0058]** There is one more reason why particulate silicas may not be the preferred forms of silica, including forms of particulate silica with internal porosity and hence high pore volume. It is well know from the literature (e.g., Wachs et al., J. Cat. 161, 211-221 (1996)) that silica, by itself, is not a good support for vanadia SCR catalysts, while titania and tungsta-doped titania are good supports. Hence, it may be desirable to minimize the amount of silica surface area that is available to adversely interact with vanadia, while maximizing the amount of $TiO_2/WO_3$ surface area, so as to make the most active catalyst. Thus, only enough silica is used to stabilize the titania, and it is used in a form (molecularly dispersed on the titania surface) that has minimal adverse impact on the vanadia catalyst.

**[0059]** Finally, another approach to make the materials, wherein the particulate forms of silica described above can be used, is now described. It is well known that particulate amorphous silica is soluble to an extent that depends on solution pH and temperature, see for example Iler, (op cit., p. 42). Above about pH 9 and for temperatures

higher than ambient temperature, amorphous silica will appreciably dissolve. This dissolved silica can then be precipitated again, for example onto a titania surface, by subsequently lowering the temperature and/or pH to a region that has lower silica solubility. In this manner, particulate silicas that are finely mixed with anatase titania can be dissolved and redistributed in a well-dispersed manner onto the titania surface via the hydrothermal treatment. However, such a post-treatment is not a preferred method of making the compositions, since this step adds processing time and cost during the mixed oxide manufacture. It is most preferred to use a suitable silica precursor and treat the titania directly.

**[0060] EXAMPLES**

**[0061]** Titania Starting Material

**[0062]** In one embodiment of the present invention, a sulfated titania slurry (see Table 1) was used. Such a sulfated titania slurry can be obtained as an intermediate product in a production process for making titanium dioxide using the sulfuric acid process, for example as produced by the MIC production facility in Thann, France. Such a slurry comprises about 27% of a high surface area, hydrous anatase titania, $TiO_2$. The $TiO_2$has primary crystallite particles having sizes of less than 5 nanometers, and corresponding $N_2$ BET surface areas in excess of 250 $m^2/g$. The slurry has a viscosity of 0.5-3 poises, a density of 1275 $kg/m^3$, and a low pH of around 1.5 - 2.0, which results from the fact that the slurry contains about 6.6 wt% $SO_3$. However, the present invention is not restricted to use of this slurry. Any composition comprising hydrous anatase titania could be used herein. Indeed, it is not necessary to use a sulfated titania slurry as the starting material. A dried low-sulfate anatase titania precursor could be used instead.

**[0089]** Example 6 : Silica Surface Stabilization

**[0090]** As noted elsewhere herein, a very stable ultrafine titania using a minimal amount of silica additive may be provided. As noted above, particulate silicas (e.g., colloidal, fumed, and precipitated) are not ideal sources of silica for use in titania-supported vanadium catalysts, because much of the silica is not available to interact with the titania surface. Another form of silica that could be used to more effectively stabilize the surface of the titania, but that would have a minimal adverse impact on the catalytic activity of vanadia supported on the surface of the titania is described herein.

**[0091]** The use of silica in low molecular weight and/or small nanoparticle form was considered, rather than in the particulate form which is present in the conventional amorphous silicas described above. The lowest molecular weight form of silica in aqueous solution is silicic acid, $Si(OH)_4$. However, this chemical entity has a very low solubility in water, and therefore is restricted to concentrations of a few hundred ppm. (Discussions of the aqueous chemistry of silica in water, are found for example, in Iler , (op cit.) and Brinker, C. J and Scherer, G. W, 1990, Chapter 3).

[0092] In view of the low solubility of $Si(OH)_4$, we turned to experimentation with tetra(alkyl)ammonium silicate solutions (including, but not limited to, tetramethylammonium, TMA). These reagents contain silica in low molecular weight forms (see Engelhardt and Michel, op cit.). Furthermore, the silica in these solutions is present at fairly high concentrations (e.g., 9 wt% $SiO_2$). Thus, we considered whether or not the molecular entities in these solutions may be small enough to react selectively with the titania surface, while not providing separate area for vanadia to bond which would diminish its catalytic activity.

**[0093]** $^{29}$Si NMR spectroscopy of a liquid sample of soluble silicate.

[0094] In order to determine the nature of the silicate species in commercially available TMA silicate solution, the commercial source of TMA silicate used in these examples (Alfa TMA-silicate, 9% $SiO_2$) was evaluated using $^{29}$Si NMR spectroscopy on a 400 MHz instrument by Spectral Data Services, Inc. Shown in Table 6 are the results.

What is claimed is:

1. A catalyst support material, comprising:

anatase titania particles comprising ≥ 85 wt% dry weight of $TiO_2$ 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% to 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 a silica-stabilized titania catalyst support material, 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 reprecipitated on the $TiO_2$ particles to form the 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.