Title: SELECTIVE CATALYTIC REDUCTION (SCR) CATALYST COMPRISING A COMPOSITE OXIDE CONTAINING V AND SB, PREPARATION PROCESS THEREOF, AND USE THEREOF FOR NITROGEN OXIDES REMOVAL

Abstract: A catalyst composition comprising a support comprising TiO₂, a composite oxide containing vanadium and antimony, which has a rutile-type structure different from V₂O₅ and V₂O₅₋ₓSbx (-0.7) determined by X-ray diffraction (XRD) analysis with Cu Kα radiation, and optionally, one or more selected from the group consisting of oxides of silicon, oxides of vanadium and oxides of antimony, for selective catalytic reduction of nitrogen oxides; a process for preparing the catalyst composition, to the catalyst composition obtained/obtainable by the process and to use of the same for selective catalytic reduction of nitrogen oxides.
Selective Catalytic Reduction (SCR) Catalyst Comprising a Composite Oxide containing V and Sb, Preparation Process Thereof, and Use Thereof for Nitrogen Oxides Removal

Technical Field
5 Generally, the present invention relates to a catalyst for nitrogen oxides (NOx) removal. More specifically, the present invention relates to a selective catalytic reduction (SCR) catalyst containing vanadium and antimony on a support, preparation process thereof, and use thereof for NOx removal.

Background
10 NOx emitted as exhaust gases from mobile source such as vehicles and stationary source such as a power plant would be harmful to environment and human beings. In order to remove NOx from exhaust gases, catalytic reducing methods have heretofore been developed. The catalytic reducing methods are suitable for dealing with large quantities of exhaust gases, and of these, a process comprising adding ammonia as a reducing agent to catalytically reduce NOx selectively to N2 was reported to be superior. The catalysts used in such selective catalytic reduction (SCR) are required to reduce NOx over a broad temperature range and especially at a temperature as low as possible below 300 °C.

SCR catalysts which are vanadium(V)/antimony(Sb) binary systems based on a support, such as V/Sb/TiO2 have been disclosed, for example, in KR 101065242 B1, US 2009/143225 A1 and US 4221768. It is believed that the incorporation of Sb as a promoter in conventional V-containing catalysts can result in improved SCR performance of the catalysts.

US 8975206 B2 discloses a catalyst composition comprising a vanadate represented by XVO4/S, in which XVO4 stands for Bi-, Sb-, Ga- and/or Al-vanadate, and S is a support comprising TiO2. Among others, VSB04 supported on TiO2/WO3/SiO2 is given as an example, which is prepared by mixing V and Sb source solutions, drying at 120°C and calcining at 550°C for 20 hours to obtain VSB04 which is then supported on TiO2/WO3/SiO2. No XRD pattern showing the structure of the vanadates, especially of VSB04 is disclosed in the patent.

WO 2013/179129 A2 discloses a SCR filter comprising a substrate in the form of a wall flow filter and a catalyst carried on said substrate, the catalyst comprising a support and a vanadate component. Said vanadate has a structure defined by the formula of (A)x(T)y(R2)VO4, wherein "A" is an alkaline earth metal, "T" is a transition metal, "R" is a rare earth metal, and "x", "y" and "z" are molar ratios of respective metals to vanadium with 0 ≤ x < 1, 0 < y < 1, 0 ≤ z ≤ 1 and x + y + z = 1. This patent application only discloses FeV04 as the vanadate
component. The SCR performance of the wall flow filter comprising FeV0₄ carried on the substrate is not discussed in the application.

In spite of the known SCR catalysts, there is still a need for SCR catalysts that exhibit excellent activity for NOx removal, especially in mobile and stationary exhaust gas emission applications.

**Summary of the Invention**

An object of the present invention is to provide a novel SCR catalyst with improved NOx removal, especially in mobile and stationary exhaust gas emission applications. The object can be achieved by a catalyst composition, a method for the preparation thereof, use of the catalyst composition for selective catalytic reduction of nitrogen oxides. Particularly, the present invention relates to following aspects.

1. Use of a catalyst composition comprising:
   - a support comprising Ti0₂,
   - a composite oxide containing vanadium and antimony, which has a rutile-type structure different from VSb0₄ and Vo.₉Sbo.₉₂O₂₄ as determined by X-ray diffraction (XRD) analysis with Cu Kα radiation, and
   - optionally, one or more selected from the group consisting of oxides of silicon, oxides of vanadium and oxides of antimony,
   
   for selective catalytic reduction of nitrogen oxides.

2. Use according to the above aspect 1, wherein the composite oxide containing vanadium and antimony is characterized by an XRD diffraction peak of (110) or (101) plane at higher 2θ than those of VSb0₄ and Vo.₉Sbo.₉₂O₂₄ by at least 0.1°.

3. Use according to the above aspect 2, wherein the composite oxide containing vanadium and antimony is characterized by an XRD diffraction peak of (101) plane at higher 2θ than those of VSb0₄ and Vo.₉Sbo.₉₂O₂₄ by at least 0.2°, preferably at least 0.3°, and more preferably at least 0.5°.

4. Use according to any of the above aspects 1 to 3, wherein the composite oxide containing vanadium and antimony is characterized by an XRD diffraction peak of (110) plane at 2θ in the range of from 27.25° to 29.00° and an XRD diffraction peak of (101) plane at 2θ in the range of from 35.43° to 37.00°.

5. Use according to any of the above aspects 1 to 4, wherein vanadium, including those in both the composite oxide vanadium and antimony and the optional oxide(s) of vanadium, is...
present in the catalyst composition in the range of 0.5 to 6% by weight, preferably 1 to 4.5% by weight, and more preferably 2 to 4% by weight, calculated as elemental V; and wherein antimony, including those in both the composite oxide vanadium and antimony and the optional oxide(s) of antimony, is present in the catalyst composition in the range of 0.8 to 16% by weight, preferably 3.5 to 14% by weight, and more preferably 5 to 10% by weight, calculated as elemental Sb.

6. Use according to any of the above aspects 1 to 5, wherein the catalyst composition is in a shaped form, preferably in form of extrudate, or is carried on a substrate.

7. Use according to the above aspect 1, wherein the nitrogen oxides are present in exhaust gases from an internal combustion engine such as diesel engine, a power plant or an incinerator.

8. A process for preparing the catalyst composition as defined in any of the above aspects 1 to 6, which includes steps of:

(i) mixing a vanadium/antimony oxide and optionally a silicon source with a support comprising TiO₂ in a solvent to obtain a suspension;

(ii) optionally, applying the suspension onto a substrate;

(iii) drying at a temperature in the range of 80 and 250 °C;

(iv) calcining at a temperature of at least 500 °C.

9. The process according to the above aspect 8, wherein the calcining in step (iv) is conducted at a temperature in the range of higher than 500 °C to 700 °C, more preferably 550 °C to 700 °C, still preferably 600 °C to 700 °C, and most preferably 650 °C to 700 °C.

10. The process according to the above aspect 8 or 9, wherein the vanadium/antimony oxide used in step (i) is prepared by

(a) providing a suspension comprising vanadium oxide(s) and antimony oxide(s); and

(b) drying the suspension to obtain the vanadium/antimony oxide at a temperature in the range of 80°C to 250 °C.

11. The process according to the above aspect 8 or 9, wherein the vanadium/antimony oxide used in step (i) is prepared by

(a') providing a suspension or solution comprising a vanadium source and an antimony source;

(b') precipitating and separating the vanadium/antimony oxide from the suspension or solution; and
optionally, drying at a temperature in the range of 80 °C to 250 °C.

12. The process according to any of the above aspects 8 to 11, which does not comprise step (ii), and optionally comprises a step of shaping in order to obtain the catalyst composition in a shaped form.

13. A catalyst composition obtained/obtainable by the process according to any of the above aspects 8 to 12.

14. Use of the catalyst composition according to the above aspect 13 for selective catalytic reduction of nitrogen oxides.

15. Use according to the above aspect 14, wherein the nitrogen oxides are present in exhaust gases from an internal combustion engine such as diesel engine, a power plant or an incinerator.

**Brief of the Drawings**

Figure 1 shows an XRD pattern of a catalyst composition as prepared in Example 1 according to the present invention.

Figure 2 shows an XRD pattern of a catalyst composition as prepared in Example 2 according to the present invention.

Figure 3 shows an XRD pattern of a catalyst composition as prepared in Example 3 according to the present invention.

Figure 4 shows an STEM-EDS image of a catalyst composition as prepared in Example 2 according to the present invention.

**Detailed Description of the Invention**

< Catalyst Composition>

The present invention provides a catalyst composition, comprising:

- a support comprising TiO₂,

- a composite oxide containing vanadium and antimony, which has a rutile-type structure different from VSb₀.₄ and Vo₉Sb₀.₉₂O₄ as determined by X-ray diffraction (XRD) analysis with Cu Kα radiation, and

- optionally, one or more selected from the group consisting of oxides of silicon, oxides of vanadium and oxides of antimony.

The support useful in the catalyst composition according to the present invention may be
any supports comprising TiO\(_2\). Preferably, the support consists of TiO\(_2\), of TiO\(_2\) and SiO\(_2\), of TiO\(_2\) and WO\(_3\), of TiO\(_2\) and SiO\(_2\) and WO\(_3\), of TiO\(_2\) and AI\(_2\)O\(_3\) or of TiO\(_2\) and ZrO\(_2\). More preferably, the support consists of TiO\(_2\). TiO\(_2\) to be used in the present invention may be commercially available, or may be prepared via conventional processes known in the art. In a further embodiment according to the present invention, TiO\(_2\) to be used in the present invention is in form of anatase.

In an embodiment, the composite oxide containing vanadium and antimony shows an XRD diffraction peak of (110) or (101) plane at higher 2\(\Theta\) value than those of rutile-type VSb\(_0\)\(_x\) and Vo.92Sbo.92O\(_4\) by at least 0.1°, preferably at least 0.2°, as determined by XRD analysis with Cu Ka radiation.

In the context of the present invention, any 2\(\Theta\) values of VSb\(_0\)\(_x\) and Vo.92Sbo.92O\(_4\) refer to those according to PDF 00-016-0600 for VSb\(_0\)\(_x\) and PDF 04-007-9467 for Ref. V\(_{0.92}\)Sbo.92O\(_4\), as available from 2014 PDF4 Database, International Centre for Diffraction Data, Newtown Square, Pennsylvania, U.S.A.

The XRD diffraction analysis as used in the context of the present invention refers to XRD diffraction with Cu Ka radiation, unless mentioned otherwise.

In a preferable embodiment, the composite oxide containing vanadium and antimony shows an XRD diffraction peak of (101) plane at higher 2\(\Theta\) than those of VSb\(_0\)\(_x\) and Vo.92Sbo.92O\(_4\) by at least 0.1°, preferably at least 0.2°, more preferably at least 0.3°, even more preferably at least 0.5°, and most preferably at least 0.7°.

In a particularly preferable embodiment, the composite oxide containing vanadium and antimony is characterized by an XRD diffraction peak of (110) plane at 2\(\Theta\) in the range of from 27.25° to 29.00° and an XRD diffraction peak of (101) plane at 2\(\Theta\) in the range of from 35.43° to 37.00°.

Without being bound by any theories, it is assumed that the composite oxide containing vanadium and antimony may be represented by an empirical formula VSb\(_a\)Ti\(_b\)O\(_c\), in which \(a\) is the molar ratio of Sb to V and has a value of from more than 0 to less than 1, \(b\) is the molar ratio of Ti to V and has a value of 0 to less than 1, and \(c\) is the molar ratio of O to V and is determined by the valence requirements of the elements present. In a particular embodiment, titanium is present together with vanadium and antimony in the composite oxide having a rutile-type structure, i.e. \(b > 0\). In a further embodiment, the sum of the index \(a\) and the index \(b\) in formula VSb\(_a\)Ti\(_b\)O\(_c\) is ≤1.

In a further particular embodiment, the composite oxide containing vanadium and antimony does not contain silicon. In other words, silicon is not present in the rutile-type
structure of the composite oxide.

The content of vanadium present in the catalyst composition according to the present invention, including those in both composite oxide containing vanadium and antimony and the optional oxide(s) of vanadium, is preferably in the range of 0.5 to 6% by weight, preferably 1 to 4.5% by weight, and more preferably 2 to 4% by weight, calculated as elemental V. The content of antimony present in the catalyst composition according to the present invention, including those in both composite oxide containing vanadium and antimony and the optional oxide(s) of antimony, is preferably in the range of 0.8 to 16% by weight, preferably 3.5 to 14% by weight, and more preferably 5 to 10% by weight, calculated as elemental Sb.

The content of silicon (if present) in the catalyst composition according to the present invention is preferably in the range of 0.2 to 9.5% by weight, preferably 0.4 to 7% by weight, more preferably 0.9 to 4.6% by weight, calculated as elemental Si.

The content of titanium calculated as TiO₂, including those present in the support and those possibly present in the composite oxide containing vanadium and antimony is preferably in the range of 50 to 97.5% by weight, preferably 61 to 93% by weight, and more preferably 73 to 90% by weight, based on the total weight of the catalyst composition according to the present invention.

The catalyst composition according to the present invention can be used in a powder form or in a shaped form. For example, catalyst composition according to the present invention may be shaped into beads, spheres, pellets, or crushed particles and the like, according to various techniques known in the art. It is to be understood that any conventional matrix materials or auxiliary agents may be incorporated during the shaping process as desired and thus may be comprised in the shaped form of the catalyst composition according to the present invention.

Alternatively, the catalyst composition according to the present invention may be applied on a substrate. The substrate is not particularly limited, and for example, a honeycomb substrate or a wall-flow substrate. The substrate may be any of those materials typically used for preparing catalysts, such as ceramic or metal.

In a preferable embodiment, the present invention provides a catalyst composition which is carried on a substrate as a washcoat, wherein the catalyst composition comprises:

- a support comprising TiO₂,

- a composite oxide containing vanadium and antimony, which has a rutile-type structure different from VSb0.4 and Vo.9Sb0.92O4 as determined by X-ray diffraction (XRD) analysis with Cu Kα radiation, and

- optionally, one or more selected from the group consisting of oxides of silicon, oxides
of vanadium and oxides of antimony.

In a preferable embodiment, the substrate comprises a ceramic or metal honeycomb structure. Any suitable substrate may be employed, such as a monolithic substrate of the type having fine, parallel gas flow passages extending therethrough from an inlet or an outlet face of the substrate. The passages, which are essentially straight paths from their fluid inlet to their fluid outlet, are defined by walls on which the catalyst composition is carried as a washcoat so that the gases flowing through the passages contact the catalyst composition. The flow passages of the monolithic substrate are thin-walled channels, which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, circular, etc.

Such monolithic substrates may contain up to about 900 or more flow passages (or "cells") per square inch of cross section, although far fewer may be used. For example, the substrate may have from about 50 to 600, more usually from about 200 to 400, cells per square inch ("cpsi"). The cells can have cross sections that are rectangular, square, circular, oval, triangular, hexagonal, or are of other polygonal shapes.

Preferably, the catalyst composition may be loaded on the substrate in an amount of 1-10 g/in³, and preferably 1-7 g/in³, and more preferably 2-5.5 g/in³.

The catalyst composition according to the present invention can be used for reducing nitrogen oxides (NOx), especially in exhaust gas from an internal combustion engine or from power plant, as described hereinafter.

It is to be understood that the contents of the support and the components in each case are calculated relative to the total weight of the catalyst composition according to the present invention, the substrate if present being not included in the said total weight, unless mentioned otherwise.

<Process for Preparing the Catalyst Composition>

In a further aspect of the invention, a process for preparing the catalyst composition according to the present invention is provided, which includes steps of:

(i) mixing a vanadium/antimony oxide and optionally a silicon source with a support comprising TiO₂ in a solvent to obtain a suspension;

(ii) optionally, applying the suspension onto a substrate;

(iii) drying at a temperature in the range of 80 and 250 °C;

(iv) calcining at a temperature of at least 500 °C.
In the context of the invention, the vanadium/antimony oxide is intended to mean a mixture of vanadium oxide(s) and antimony oxide(s), an oxide of vanadium and antimony, or a combination of an oxide(s) of vanadium and antimony with a mixture of vanadium oxide(s) and antimony oxide(s).

In the process according to the present invention, the silicon source, when used, is not particularly limited, preferably selected from the group consisting of silicic acid, silica sol, quartz, fused or amorphous silica, silicates such as sodium silicate, alkoxy silanes, silicone resins, etc. or a combination of any two or more thereof.

The description hereinabove as to the support for the catalyst composition applies to the process according to the present invention.

In an embodiment of the process according to the present invention, the vanadium/antimony oxide used in step (i) is prepared by

(a) providing a suspension comprising vanadium oxide(s) and antimony oxide(s); and

(b) drying the suspension to obtain the vanadium/antimony oxide at a temperature in the range of 80 °C to 250 °C.

In this embodiment, the vanadium oxide(s) and antimony oxide(s) used in step a) are not particularly limited, for example V₂O₅ and Sb₂O₃ can be used.

In a further embodiment of the process according to the present invention, the vanadium/antimony oxide used in step (i) is prepared by

(a') providing a suspension or solution comprising a vanadium source and an antimony source;

(b') precipitating and separating the vanadium/antimony oxide from the suspension or solution; and

(c') optionally, drying at a temperature in the range of 80 °C to 250 °C.

In the context of the invention, the vanadium source and antimony source are intended to mean compounds containing vanadium and compounds containing antimony, respectively, which may be converted to the vanadium/antimony oxide in the process.

In this embodiment, the vanadium source is preferably selected from the group consisting of ammonium vanadate, vanadyl oxalate, vanadium pentoxide, vanadium monoethanolamine, vanadium chloride, vanadium trichloride oxide, vanadyl sulfate, vanadium antimonite, vanadium antimonate and vanadium oxides. The antimony source is preferably selected from the group consisting of antimony acetate, ethylene glycol antimony, antimony sulfate, antimony nitrate, antimony chloride, antimonous sulfide, antimony oxides and antimony
vanadate.

In the process according to the present invention, the solvent used in step (i) and the solvent in the suspension or solution in step (a) and (a’) independently of each other, may be any suitable solvents known in the art, preferably a solvent comprising water, preferably the solvent being DI water.

In step (ii) of the process according to the present invention, the suspension is optionally applied onto the substrate by any methods known in the art. For example, the lower end of the substrate may be dipped into the suspension, and vacuum is applied to the upper end of the substrate, so that the suspension is drawn into the passages of the substrate to a desired length. The description hereinabove as to the substrate to carry the catalyst composition applies to the process according to the present invention.

In step (iii) of the process according to the present invention, the suspension from step (i) or the obtained substrate from step (ii) is dried at a temperature in the range of 80 °C to 250 °C, preferably 100 °C to 200 °C, more preferably 100 °C to 150 °C. The drying can be conducted in any ways known in the art without particular limitations.

The preferable temperature ranges discussed above are also applicable to step (b) and step (c’) in respective embodiments of the process according to the present invention. The drying in those steps can also be conducted in any ways known in the art without particular limitations, with spray drying being preferable.

In step (iv) of the process according to the present invention, the calcining is preferably conducted at a temperature in the range of 500 °C to 700 °C, preferably in the range of higher than 500 °C to 700 °C, more preferably 550 °C to 700 °C, even more preferably 600 °C to 700 °C, and most preferably 650 °C to 700 °C.

According to an embodiment of the process according to the present invention, if appropriate, the precipitating in step (b’) is conducted in the presence of a precipitator, e.g., ammonia, ammonium bicarbonate, ammonium carbonate, sodium hydroxide, potassium hydroxide, sodium carbonate, and etc.

Any other conventional additives such as dispersant, binder and/or thickener may be used during the process according to the present invention, if desired.

In a further embodiment, the process according to the present invention does not comprise applying the suspension from step (i) onto a substrate, which optionally comprises a step of shaping instead in order to obtain the catalyst composition in a shaped form. Shaping, when desired, is carried out before the calcining step (iv), preferably before the drying step (iii). It is to be understood that any conventional matrix materials or auxiliary agents may be
incorporated during the shaping process as desired.

< Method for Selective Catalytic Reduction of Nitrogen Oxides (NOx) in Exhaust Gas>

In a further aspect, the present invention relates to use of the catalyst composition according to the present invention or the catalyst composition obtained/obtainable by the process according to the present invention for selective catalytic reduction of NOx, especially in exhaust gases.

The exhaust gases which can be treated by the catalyst composition according to the present invention or the catalyst composition obtained/obtainable by the process according to the present invention are any exhaust gases containing NOx to be removed or reduced. The exhaust gases are from for example, but not limited to an internal combustion engine, a power plant or an incinerator.

Accordingly, a method for reducing NOx in exhaust gas from an internal combustion engine is provided, comprising contacting the exhaust gas with the catalyst composition according to the present invention or the catalyst composition obtained/obtainable by the process according to the present invention.

In a particular embodiment, the exhaust gases are contacted with the catalyst composition according to the present invention or the catalyst composition obtained/obtainable by the process according to the present invention at a temperature in the range of 150 °C to 650 °C, or 180 to 600 °C, or 200 to 550 °C.

The contact of the exhaust gases with the catalyst composition according to the present invention or the catalyst composition obtained/obtainable by the process according to the present invention is conducted in the presence of a reductant. The reductant that can be used in the present invention may be any reductants known in the art per se for reducing NOx, for example NH₃, NH₄ may be derived from urea.

There may be other catalyst(s) upstream or downstream in the flow direction of the exhaust gases.

In a preferred embodiment of the invention, the internal combustion engine is a diesel engine.

The invention will be further illustrated by the following Examples, which set forth particularly advantageous embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.
Examples

Preparation of vanadium/antimony oxide — compound 1

40.0 g V2O5 and 64.1 g Sb2O3 were mixed in 300 g DI water, and agitated to form a suspension. This suspension was spray dried at 200 °C to form a mixture of oxides with a molar ratio V : Sb of 1 : 1.

Example 1

10.4 g Compound 1 was added in 100.0 g DI water, and then stirred for 30 min, followed by addition of 84.6 g TiO2 powder and 16.7 g aqueous colloidal SiO2 solution (30% SiO2 solid). The thus-obtained suspension was applied onto a 400/6 honeycomb cordierite substrate (with number 400 referring to cells per square inch (cpsi) and 6 referring to wall thickness between channels in mils), dried at a temperature of 120 °C overnight, followed by calcination at 500 °C for 3h in air. After cooling to room temperature, Catalyst 1 was obtained. The total loading of washcoat on the substrate is 3.0 g/in³.

Example 2

Example 1 was repeated, except that the calcination was carried out at 650 °C for 3 h to obtain Catalyst 2.

Example 3

Example 1 was repeated, except that the calcination was carried out at 700 °C for 3 h to obtain Catalyst 3.

Example 4

13.0 g Compound 1 was added in 100.0 g DI water, and then stirred for 30 min, followed by addition of 82.0 g TiO2 powder and 16.7 g aqueous colloidal SiO2 solution (30% SiO2 solid). The thus-obtained suspension was applied onto a 400/6 cpsi honeycomb cordierite substrate, dried at a temperature of 120 °C overnight, followed by calcination at 500 °C for 3h in air. After cooling to room temperature, Catalyst 4 was obtained. The total loading of washcoat on the substrate is 3.0 g/in³.

Example 5

Example 4 was repeated, except that the calcination was carried out at 650 °C for 3 h to obtain Catalyst 5.

Example 6

Example 4 was repeated, except that the calcination was carried out at 700 °C for 3 h to obtain Catalyst 6.
The washcoats of Catalysts 1 to 3 as obtained in the above Examples were characterized by XRD analysis with Cu Ka radiation, step size 0.02°, D8 Advance Series II, Bruker AXS GmbH. The XRD patterns of Catalysts 1, 2 and 3 are shown in Figures 1, 2 and 3 respectively. The rutile-type structure's XRD data together with cell parameters of the washcoats of Catalysts 1 to 3 and those of Vo.92Sbo.92O4 and VSb0 4 are summarized in Table 1.

Table 1. XRD data of VSb0 4 and Vo.92Sbo.92O4 and of the washcoats of Catalysts 1 to 3

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rutile-related 20 (°) (110)</th>
<th>Rutile-related 20 (°) (101)</th>
<th>Rutile-related a (Å)</th>
<th>Rutile-related c (Å)</th>
<th>TiO2 anatase 20 (°) (101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. VSbO4 (PDF: 00-016-0600)*</td>
<td>27.420</td>
<td>35.093</td>
<td>4.598</td>
<td>3.078</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Ref. V0.92Sb0.02O4 (PDF: 04-007-9467)*</td>
<td>27.267</td>
<td>35.329</td>
<td>4.622</td>
<td>3.038</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Catalyst 1 (500 °C/3h)</td>
<td>27.306</td>
<td>35.375</td>
<td>4.615</td>
<td>3.034</td>
<td>25.30</td>
</tr>
<tr>
<td>Catalyst 2 (650 °C/3h)</td>
<td>27.434</td>
<td>36.025</td>
<td>4.594</td>
<td>2.965</td>
<td>25.29</td>
</tr>
<tr>
<td>Catalyst 3 (700 °C/3h)</td>
<td>27.349</td>
<td>35.863</td>
<td>4.608</td>
<td>2.979</td>
<td>25.29</td>
</tr>
</tbody>
</table>

* 2014 PDF4 Database, International Centre for Diffraction Data, Newtown Square, Pennsylvania, U.S.A.

The 2Θ values of TiO2 anatase (101) plane are the same among Catalysts 1 to 3, and consistent with the known 2Θ values of TiO2 anatase (101) plane. It is believed that the XRD patterns and data regarding the rutile-type structures of the Catalysts 1 to 3 are reliable.

It can be seen from the XRD patterns shown in Figures 1 to 3 and the data given in Table 1, the washcoat of Catalyst 1 shows similar XRD diffractions (2Θ values) and cell parameters (a, c values) to Ref. Vo.92Sbo.92O4. In contrast, diffraction peaks of (101) planes of the washcoats of Catalyst 2 and Catalyst 3 shift to higher 2Θ values than those of Ref. VSb0 4 and Ref. Vo.92Sbo.92O4 by at least 0.5°, and the rutile-related parameter c values for Catalyst 2 and Catalyst 3 are clearly smaller than Ref. VSb0 4 and Ref. Vo.92Sbo.92O4. It shows that Catalyst 2 and Catalyst 3 contain a TiO2 anatase structure and a composite oxide rutile-type structure different from Vo.92Sbo.92O4 and VSb0 4.

Catalyst 2 was also analyzed by Scanning Transmission Electron Microscopy—Energy Dispersive Spectroscopy (STEM-EDS), with FEI Magellan 400 Scanning Electron Microscope, FEI Company, coupled with an X-Max N 80 mm2 EDS Detector, Oxford Instruments. A sample was dispersed ultrasonically in ethanol, dropped onto a copper web
covered with carbon film, and then subjected to STEM microscopic structure analysis under a voltage of 30 kV. The STEM-EDS image as shown in Figure 4 depicts distributions of V and Sb over TiO$_2$ are almost the same while distribution of SiO$_2$ is different or independent. This suggests that Si is not incorporated in the rutile-type structure.

**SCR activity test of Catalysts 1 to 6**

Catalysts 1 to 6 were tested for NOx removal in terms of SCR activity. All the catalysts were placed in the fixed bed lab simulator for testing. 7 g catalyst in cylinder shape with diameter of 1 inch and length of 3 inch was used in each testing. The feed gas consists of 500 ppm NH$_3$, 500 ppm NO, 5 % H$_2$O, 10 % O$_2$ and a balance of N$_2$. Space velocity is 60,000 h$^{-1}$. The activity test results are summarized in Table 2.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>NOx conversion @250°C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (500 °C/3h)</td>
<td>16.7</td>
</tr>
<tr>
<td>2 (650 °C/3h)</td>
<td>73.9</td>
</tr>
<tr>
<td>3 (700 °C/3h)</td>
<td>78.5</td>
</tr>
<tr>
<td>4 (500 °C/3h)</td>
<td>21.7</td>
</tr>
<tr>
<td>5 (650 °C/3h)</td>
<td>83.6</td>
</tr>
<tr>
<td>6 (700 °C/3h)</td>
<td>50.4</td>
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</tbody>
</table>

Catalysts 1 to 3 were prepared from the same starting material formulation and differ from each other only in the calcination temperature during the preparation. It can be seen that Catalysts 2 and 3 obtained under higher calcination temperatures (650 °C and 700 °C, respectively) showed significantly higher NOx conversion, compared with Catalyst 1. It is assumed that Catalysts obtained under a calcination temperature higher than 500 °C contain the composite oxide having a rutile-type structure different from V$_{0.9}$Sb$_{0.4}$O$_4$ and VSb$_{0.4}$ as characterized by XRD analysis. Comparisons of Catalysts 4 vs. 5 and 6 also show the positive effect of the composite oxide obtained under higher calcination temperatures on the SCR activity of the catalysts.

**Comparative Examples**

For comparison, more catalyst compositions were prepared.

**Comparative Example 1**
10.4 g Compound 1 which has been pre-treated at 550 °C for 20h was added in 100.0 g DI water, and then stirred for 30 min, followed by addition of 84.6 g TiO₂ powder and 16.7 g aqueous colloidal SiO₂ solution (30% SiO₂ solid). The thus-obtained suspension was applied onto a 400/6 honeycomb cordierite substrate, dried at a temperature of 120 °C overnight, followed by calcination at 650 °C for 3h in air. After cooling to room temperature, Comparative Catalyst 1 was obtained. The total loading of washcoat on the substrate is 3.0 g/m³.

**Comparative Example 2**

Comparative Example 1 was repeated, except that the calcination was carried out at 700 °C for 3h, to obtain Comparative Catalyst 2.

**Comparative Example 3**

In a typical synthetic process, 22.73 g vanadyl oxalate solution (11% V₂O₅ solid) was added in 100.0 g DI water, and then mixed with 16.7 g aqueous colloidal SiO₂ solution (30% SiO₂ solid). The mixture was stirred for 30 min, followed by addition of 92.5 g WO₃/TiO₂ powder. The resulting paste was diluted by DI water. Then the thus-obtained slurry was coated onto a 400/6 honeycomb cordierite substrate, and dried at 120 °C overnight, followed by calcination at 450 °C for 3h in air. After cooling to room temperature, Comparative Catalyst 3 was obtained.

**SCR activity test of Comparative Catalysts 1 to 6**

The Comparative Catalysts were tested via the procedure as described above and the activity test results are summarized in Table 3.

<table>
<thead>
<tr>
<th>Comparative Catalysts</th>
<th>NOx Conversion @ 250 °C, %</th>
</tr>
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<tbody>
<tr>
<td>1 (pre-treatment @550 °C/20h and calcination @650 °C/3h)</td>
<td>54.1</td>
</tr>
<tr>
<td>2 (pre-treatment @550 °C/20h and calcination @700 °C/3h)</td>
<td>65.1</td>
</tr>
<tr>
<td>3 (V₂O₅/SiO₂ supported on WO₃/TiO₂)</td>
<td>73.5</td>
</tr>
</tbody>
</table>

The preparation of Comparative Catalyst 1 differs from the preparation of Catalyst 2 only in that Compound 1 was pre-treated at a temperature of 550 °C for 20 h before mixed with...
other components. Catalyst 2 shows much higher NOx conversion than Comparative Catalyst 1. Similarly, Catalyst 3 showed higher NOx conversion than Comparative Catalyst 2. It is assumed that TiO₂ as the support facilitates or participates in the formation of the composite oxide containing vanadium and antimony during a high temperature calcination, which composite oxide allow improved SCR activity of the catalyst composition.

Furthermore, the catalyst composition according to the present invention or the catalyst composition obtained/obtainable by the process according to the present invention even showed superior performance in terms of SCR activity to the Comparative Catalyst 3, which is a typical commercially available SCR catalyst.

While this invention has been described in connection with what is presently considered to be practical exemplary embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.
Claims

1. Use of a catalyst composition comprising:
   - a support comprising TiO₂,
   - a composite oxide containing vanadium and antimony, which has a rutile-type structure different from VSb₀.⁴ and Vo.₉Sbo.₉2O₄ as determined by X-ray diffraction (XRD) analysis with Cu Kα radiation, and
   - optionally, one or more selected from the group consisting of oxides of silicon, oxides of vanadium and oxides of antimony,

   for selective catalytic reduction of nitrogen oxides.

2. Use according to claim 1, wherein the composite oxide containing vanadium and antimony is characterized by an XRD diffraction peak of (110) or (101) plane at higher 2Θ than those of VSb₀.⁴ and Vo.₉Sbo.₉2O₄ by at least 0.1°.

3. Use according to claim 2, wherein the composite oxide containing vanadium and antimony is characterized by an XRD diffraction peak of (101) plane at higher 2Θ than those of VSb₀.⁴ and Vo.₉Sbo.₉2O₄ by at least 0.2°, preferably at least 0.3°, and more preferably at least 0.5°.

4. Use according to any of claims 1 to 3, wherein the composite oxide containing vanadium and antimony is characterized by an XRD diffraction peak of (110) plane at 2Θ in the range of from 27.25° to 29.00° and an XRD diffraction peak of (101) plane at 2Θ in the range of from 35.43° to 37.00°.

5. Use according to any of claims 1 to 4, wherein vanadium, including those in both the composite oxide vanadium and antimony and the optional oxide(s) of vanadium, is present in the catalyst composition in the range of 0.5 to 6% by weight, preferably 1 to 4.5% by weight, and more preferably 2 to 4% by weight, calculated as elemental V; and wherein antimony, including those in both the composite oxide vanadium and antimony and the optional oxide(s) of antimony, is present in the catalyst composition in the range of 0.8 to 16% by weight, preferably 3.5 to 14% by weight, and more preferably 5 to 10% by weight, calculated as elemental Sb.

6. Use according to any of claims 1 to 5, wherein the catalyst composition is in a shaped form, preferably in form of extrudate, or is carried on a substrate.

7. Use according to claim 1, wherein the nitrogen oxides are present in exhaust gases from an internal combustion engine such as diesel engine, a power plant or an incinerator.

8. A process for preparing the catalyst composition as defined in any of claims 1 to 6,
which includes steps of:

(i) mixing a vanadium/antimony oxide and optionally a silicon source with a support comprising TiO₂ in a solvent to obtain a suspension;

(ii) optionally, applying the suspension onto a substrate;

(iii) drying at a temperature in the range of 80 and 250 °C;

(iv) calcining at a temperature of at least 500 °C.

9. The process according to claim 8, wherein the calcining in step (iv) is conducted at a temperature in the range of higher than 500 °C to 700 °C, more preferably 550 °C to 700 °C, still preferably 600 °C to 700 °C, and most preferably 650 °C to 700 °C.

10. The process according to claim 8 or 9, wherein the vanadium/antimony oxide used in step (i) is prepared by

(a) providing a suspension comprising vanadium oxide(s) and antimony oxide(s); and

(b) drying the suspension to obtain the vanadium/antimony oxide at a temperature in the range of 80°C to 250 °C.

11. The process according to claim 8 or 9, wherein the vanadium/antimony oxide used in step (i) is prepared by

(a') providing a suspension or solution comprising a vanadium source and an antimony source;

(b') precipitating and separating the vanadium/antimony oxide from the suspension or solution; and

(c') optionally, drying at a temperature in the range of 80 °C to 250 °C.

12. The process according to any of claims 8 to 11, which does not comprise step (ii), and optionally comprises a step of shaping in order to obtain the catalyst composition in a shaped form.

13. A catalyst composition obtained/obtainable by the process according to any of claims 8 to 12.

14. Use of the catalyst composition according to claim 13 for selective catalytic reduction of nitrogen oxides.

15. Use according to claim 14, wherein the nitrogen oxides are present in exhaust gases from an internal combustion engine such as diesel engine, a power plant or an incinerator.
Figure 2

A: TiO₂
B: Composite Oxide
Figure 3

A: TiO$_2$
B: Composite Oxide
Figure 4
INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2016/091711

A. CLASSIFICATION OF SUBJECT MATTER
B01J 23/00(2006.01)i; B01D 53/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J 23/-; B01D 53/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CNTXT;CNABS;VEN;DWPL;SIPOABS;selective catalytic reduction, vanadium antimony,V205,Sb203, SiO2, silicon dioixde, catalyst,TiO2,titanium dioxide,denitrat+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
19 September 2016

Date of mailing of the international search report
29 September 2016

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Form PCT/ISA/210 (second sheet) (July 2009)
# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

**International application No.**

**PCT/CN2016/001711**

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