The invention relates to a process for the preparation of a titania/metal vanadate based catalyst composition, comprising the steps of bringing into contact an amount of metatitamic acid which is sufficient to yield an amount of 60 wt.% to 99 wt.% of titania in the composition with an amount of one or more metal vanadates of the general formula Me Van(I) which is sufficient to yield an amount of 0.1 wt.% to 25 wt.% of Me Van in the composition, wherein Me denotes Mg, Ca, Sr, Ba, Zr, Mn, Fe, Cu, Ag, Al, Bi, Sb, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Yb, or individual mixtures thereof, and Van denotes VO₂⁺, V₂O₇⁺ for mixtures thereof, to form an intimate mixture, and calcining the mixture obtained. The invention further relates to the use of metatitamic acid for the preparation of a titania/metal vanadate based catalyst in a one pot reaction.
Process for the preparation of Titania/Metal Vanadate based catalyst compositions

The present invention relates to the preparation of titania/metal vanadate based catalyst compositions which are e.g. useful for the production of Selective Catalytic Reduction (SCR) catalysts for the removal of NO\textsubscript{x} in exhaust gases.

Background of the invention

The most widely employed technology for removal of NO\textsubscript{x} from exhaust gases is S(elective) C(atalytic) R(eduction), e.g. as described in O. Krocher, Chapter 9 in «Past and Present in DeNOx Catalysis», edited by P. Granger et al. published by Elsevier, wherein NO\textsubscript{x} is described to be removed by reaction with ammonia and oxygen and conversion into nitrogen and water according to the reaction

\[ 4 \text{NO} + 4 \text{NH}_3 + 0_2 = 4 \text{N}_2 + 6 \text{H}_2\text{O} \]

For many SCR-applications particularly in stationary applications mainly Ti0\textsubscript{2}vanadia compositions are used to remove NO emissions.

Processes for the preparation of Ti0\textsubscript{2}vanadia compositions which additionally may contain oxides from transition metals, Rare Earths metals and other elements and their application in SCR catalysts are disclosed in numerous publications.

In US 4,085,193 for example, catalyst compositions and various preparation processes therefore are described, wherein the catalyst compositions contain as active ingredients oxides from titanium, at least one of molybdenum, tungsten, iron, vanadium, nickel, cobalt, copper, chromium and uranium, and as optional component(s) tin and/or at least one of silver, beryllium, magnesium, zinc, boron, aluminium, yttrium, Rare Earth metal, silicon, niobium, antimony, bismuth, manganese, thorium and zirconium, which oxides are present as an intimate mixture. For example in column 44, example X-1 there is reported the synthesis of a Ti0\textsubscript{2}/W0\textsubscript{3}/V\textsubscript{2}O\textsubscript{5} catalyst by converting TiCl\textsubscript{4} into a wet cake of Ti-Hydroxide, adding ammonium paratungstate and ammonium metavanadate and calcining the final mixture to yield the catalyst. Such a catalyst may be commercially used in stationary application but also in mobile applications (e.g. in trucks).

Furthermore, a process for the preparation of a Ti0\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} catalyst starting from metatitanic acid (MTA) is described. E.g. in example IV-4 in column 32 the use of MTA which is
processed together with ammonium metavanadate (AMV) to produce a TiO$_2$/V$_2$O$_5$ catalyst is disclosed. In addition, in example XV—1 (column 51) the preparation of a TiO$_2$/V$_2$O$_5$/Fe$_2$O$_3$ catalyst is reported, starting from MTA and calcining a mixture of MTA, AMV and Fe-hydroxide to form the catalyst composition.

TiO$_2$/W0$_3$/V$_2$O$_5$ catalysts are considered nowadays as "conventional VWT-catalysts". The main disadvantage of such vanadium based catalyst type is the limited stability at temperatures above 550°C.

For example, in US 6,805,849, column 2 a TiO$_2$AVO$_3$/V$_2$O$_5$ suitable SCR catalyst for NO$_x$ removal of diesel-powered vehicles is disclosed. Although such a catalyst has shown good performance it was found that sustained high temperature operation can cause catalyst deactivation.

An improvement in terms of the thermal stability of a TiO$_2$/W0$_3$ based "SCR catalyst" is reported in EP 1 682 266 Bl. The catalysts are made by introducing a Rare Earth vanadate (REVO$_4$) into the TiO$_2$/W0$_3$ (SiO$_2$) support followed by calcination of the mixture. The vanadium in the formulations based on TiO$_2$/W0$_3$ (SiO$_2$) is present not in form of vanadium pentaoxide (V$_2$O$_5$) but in form of a Rare Earth vanadate (REVO$_4$). Such catalysts are described to be heat stable when heat treated at 750°C for 10 hours.

In US 8,465,713, column 5, line 25 there is disclosed a process for making temperature stable TiO$_2$ based "vanadate catalysts" by suspending a TiO$_2$ containing support material and a transition metal vanadate or a mixed transition metal / Rare Earth vanadate in water, evaporating the water, drying the mixture and calcining the dried mixture under air. For making the above described catalyst the TiO$_2$ containing support material has to be made in a separate process before being processed in a second step with the vanadate.

US 2013/0040808 discloses on page 3 paragraph [63] to [67] a process for making a thermally stable catalyst powder by introducing Al-, Bi-, Sb-, galliumvanadates or mixtures of Al-vanadate with Bi-vanadate, a mixture of Al-vanadate with Er-vanadate a mixture of Al-vanadate or Bi-vanadate with Fe-vanadate and Er-vanadate to a TiO$_2$ comprising support yielding thermally stable catalyst materials. Again also for this process the TiO$_2$ comprising support has to be made in a separate process before being contacted with the vanadate.

Further processes for the manufacture of SCR catalyst compositions are known from CN 103894184 and CN 103977790.
As a summary of the state of the art review it may be concluded that temperature stable TiO\textsubscript{2}metal vanadate based SCR-materials are always made using a TiO\textsubscript{2}-Containing support which is brought into contact with the vanadate. To perform such a process it is inevitable to produce the TiO\textsubscript{2} containing support prior to contacting with the metal vanadates. Thus, a two step synthesis process is required which always includes the preparation and isolation of the TiO\textsubscript{2} support prior to the second process step for preparing the vanadate catalyst and thus is more complex compared to any one-step synthesis procedure.

Summary of the invention

Surprisingly now a process for the preparation of titania/metal vanadate based catalyst compositions was found wherein the isolation of the titania support before forming the catalyst composition may be avoided.

The present invention thus provides in one aspect a process for the preparation of a titania/metal vanadate based catalyst composition, comprising the steps of bringing into contact an amount of metatitanic acid which is sufficient to yield an amount of 60 wt.% to 99 wt.% of titania in the composition with an amount of one or more metal vanadates of the general formula

$$\text{MeVan} \quad (I)$$

which is sufficient to yield an amount of 0.1 wt.% to 25 wt.% of MeVan in the composition wherein Me denotes Mg, Ca, Sr, Ba, Zr, Mn, Fe, Cu, Ag, Al, Bi, Sb, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Yb, or individual mixtures thereof, preferably Al, Fe, Zr, Ce, Pr, Nd, Gd, Dy or Er, or individual mixtures thereof, more preferably Al, Fe, Ce, Gd, Dy or Er, or individual mixtures thereof, and Van denotes V\textsubscript{2}O\textsubscript{4}\textsuperscript{2+}, V\textsubscript{2}O\textsubscript{7-}, or mixtures thereof, to form an intimate mixture and calcining the mixture obtained.

The skilled artisan is aware of the fact that Mg, Ca, Sr, Ba, Zr, Mn, Cu form divanadates, i.e. vanadates with the counter ion V\textsubscript{2}O\textsubscript{7-}, while Fe, Ag, Al, Bi, Sb, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er and Yb form orthovanadates, i.e. vanadates with the counter ion V\textsubscript{2}O\textsubscript{4}\textsuperscript{3-}.

A catalyst composition provided by a process of the present invention is e.g. useful for the production of Selective Catalytic Reduction (SCR) catalysts.
In another aspect the present invention provides a process for the preparation of a
titania/metal vanadate based catalyst composition comprising
a) providing metatitanic acid in dried form or in suspended form in a liquid, preferably
water,
b) adding the metal vanadate of the general formula I as defined above,
c) forming an intimate mixture of the compounds of a) and b),
d) removing suspension liquid from a mixture of c), if present, and
e) calcining the resulting solid.

In a process of the present invention the amount of MeVan that is brought into contact with
the metatitanic acid is sufficient so that the catalyst composition prepared comprises a
MeVan of formula I in an amount of 0,1% to 25% by weight related to the weight of the total
composition, preferably 0.5% to 15% by weight.

In a process of the present invention the amount of metatitanic acid that is brought into
contact with the MeVan is sufficient so that the catalyst composition prepared comprises a
titania in an amount of 60 to 99% by weight related to the weight of the total composition,
preferably 60 wt.% to 95 wt.%, more preferably 65 wt.% to 90 wt.%, most preferably
70 wt.% to 85 wt.%.

In a further aspect, the present invention provides a process of the present invention, wherein
additionally ammonium metavanadate and/or ammonium polyvanadate is added.

Ammonium metavanadate and/or ammonium polyvanadate, if added, preferably is/are added
before step e), in one particular embodiment after step b), preferably before step c).

Metatitanic acid is widely used on industrial scale and is available from several suppliers. A
synthesis procedure for metatitanic acid is for example disclosed in US 2,344,553.

Ammonium meta and/or ammonium polyvanadate are known compounds and may be
prepared as appropriate.

Metal vanadates of formula I which are useful in a process of the present invention are
known and may be prepared as appropriate, e.g. according to a method as disclosed in EP 1
682 266, US 8,465,713, US 2013/0040808, US 8,337,804 (particularly for Metal ortho and
Metalpolyvanadates, see column 3, line 60), Gao et al. (Catalysis Letters 23 (1994), 321-

A mixed metal vanadate, if mentioned herein, designates a mixture of the corresponding metal vanadates, e.g. FeO$_4$Er$_4$V$_4$O$_{21}$ designates a physical mixture of FeV$_4$O$_9$ and ErV$_4$O$_9$ in the molar ratio of 1:1. Such mixed metal vanadate can be prepared by combining corresponding metal vanadates, e.g. FeV$_4$O$_9$ and ErV$_4$O$_9$, e.g. by using an appropriate process, including mixing the vanadates, spray drying a mixture of vanadates, precipitating the vanadates in a co-precipitation process, etc.

In a process of the present invention removal of suspension liquid, e.g. water, may be carried out as appropriate, e.g. by distillation, evaporation or spray drying and the resulting solid may be subjected to an additional drying step before calcination. Calcination may be carried out as appropriate, e.g. according to, e.g. analogously to a method as conventional, e.g. by heating the composition obtained after solvent removal preferably in the presence of oxygen, more preferably under air, at appropriate temperatures. Appropriate temperatures include temperatures from 300°C to 900°C, more preferably from 320°C to 750°C, most preferably from 500°C to 700°C.

In order to avoid material agglomeration during calcination it may be advantageous to perform a de-agglomeration step, such as milling and/or sieving after calcination.

Beside metal vanadates, a wide variety of metal oxides which may contribute to catalytic activity, e.g. SCR catalytic activity, are known and can be optionally additionally present in the titania/metal vanadate based catalyst according to the present invention, e.g. including:

A) a metal oxide, in particular an oxide of Mg, Ca, Sr, Ba, Zr, Mn, Fe, Cu, Ag, Al, Bi, Sb, W, Mo, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Yb,
B) SiO$_2$,
C) individual mixtures of one or more oxides indicated under A) and B).

The additional metal oxides or SiO$_2$ may be added as such, or in the form of precursors which form the corresponding oxides upon heating, e.g. upon calcination.

In a further aspect the present invention provides a process according to the present invention, wherein additionally one or more metal oxides or precursors thereof, and/or SiO$_2$, or a precursor thereof are added; e.g. such as indicated above.
Such metal oxides or precursors thereof are added before step e), preferably before or after step b).

In the case of tungsten, the tungsten oxide or the precursor thereof is preferably added before step b).

In the case of metals other than tungsten and SiO₂, the metal oxides, SiO₂ or the precursors thereof are preferably added after step b), more preferably before step c).

Precursors of metal oxides which are useful in a process of the present invention include metal-carbonates, -acetates, -sulfates, -nitrates, -hydroxides, -chlorides or metal salts of any organic acid, and in case of tungsten ammonium metatungstate or ammonium paratungstate.

In another preferred embodiment the present invention provides a process comprising
- contacting in a solvent metatitanic acid with a tungsten compound, such as WO₃ or a precursor thereof, e.g. ammonium metatungstate or ammonium paratungstate, in the presence of SiO₂ or a silicium compound which forms SiO₂ after heat treatment, or in the absence of SiO₂ or a silicium compound which forms SiO₂ after heat treatment,
- adding the metal vanadate of formula (I) and forming an intimate mixture,
- removing suspension liquid from said mixture, and
- calcining the resulting solid.

In a further aspect the present invention provides a process, wherein
- the tungsten compound is used in an amount from 1% to 30%, more preferably from 3% to 5%, most preferably from 5% to 10% calculated as WO₃ in weight % based on the total weight of the catalyst composition prepared,
- the silicium compound, is used in an amount of 0% to 30%, more preferably from 1% to 30%, even more preferably from 3% to 15% and most preferably from 5% to 10% calculated as SiO₂ in weight % based on the total weight of the catalyst composition prepared.

In the process of the present invention, the amount of ammonium metavanadate and/or ammonium polyvanadate added preferably is sufficient to yield an amount of 0.3 wt% to 10% wt calculated as V₂O₅ in the composition.

The amount of metal oxide or precursor added preferably is sufficient to yield 1 wt.% to 15 wt.% of the metal oxide in the composition.
In a preferred embodiment, a metal oxide or precursor thereof is added, wherein the metal is selected from the group consisting of Cu, Mn and rare earth metals, and wherein the metal oxide or precursor thereof is added in an amount which is sufficient to yield 1 wt.% to 15 wt.% of the metal oxide in the composition.

A titania/metal vanadate based catalyst composition includes a catalyst composition which is useful to remove undesired emissions from exhaust gases. Titania/metal vanadate compositions may be used in catalyst applications for the removal of NOx, particularly in exhaust gas aftertreatment of diesel- and lean burn engines of automotives. In addition the catalyst composition may also be used in stationary applications, e.g. removal of NOx in power plant stations. preferably a titania based catalyst composition of the present invention is a SCR catalyst composition.

Surprisingly the catalyst composition prepared according to a process of the present invention exhibits an improved catalytic DeNOx activity when compared with a catalyst composition prepared according to a prior art process (see comparative example 1).

In a further aspect the process of the present invention provides a composition, comprising per 100 parts
- 65 to 85 weight parts of TiO2,
- 5 to 15 weight parts of WO3,
- 5 to 20 weight parts of one or more metal vanadates, in particular selected from ErV04, FeV04, Feo.5AlO3V04, Feo.5ErO3VO4,
- 0 to 15 weight parts of a metal oxide particularly selected from CeO2, ZrO2, V2O5, and, if desired
- 0 to 15 weight parts of SiO2;

such as
- 65 to 85, such as 70 to 82 weight parts of TiO2,
- 5 to 15, such as 8 to 12, e.g. 10 weight parts of WO3,
- 5 to 20, such as 7 to 17, e.g. 8 to 15 weight parts of a metal vanadate, preferably selected from ErV04, FeV04, Feo.5AlO3V04, Feo.5ErO3VO4,
- 0 to 15, such as 0 to 10 weight parts of a metal oxide, preferably selected from CeO2, ZrO2 and V2O5, and, if desired
- 0 to 15, such as 0 to 10 weight parts of SiO2.
In particular the process of the present invention provides a composition selected from
TiO$_2$ / WO$_3$ / ErV$_4$ ... (in the form of a powder)
ErV$_4$ was prepared according to the description [0018] disclosed in EP 1682266.

For all the above named embodiments, the amounts of TiO$_2$ and the respective MeVan in the final composition are essentially obtained by bringing into contact the necessary amounts of metatitanic acid and MeVan according to the present invention.

In another aspect the present invention provides the use of metatitanic acid for the preparation of a titania/metal vanadate based catalyst in a one pot reaction.

The catalyst compositions synthesized according to a process of the present invention are characterized by XRD-methods. In all the examples it is demonstrated that TiO$_2$ generated from MTA is present in the anatase form as a main phase after performing the process according to the present invention. Depending on the nature of the metal vanadate it is also confirmed that the vanadates may be present in crystalline or amorphous form in the catalyst compositions obtained.

In the following preferred embodiments the invention is described more in detail. The contents of the different constituents of the catalyst mixtures are expressed in weight %.

**Synthesis of Starting Materials:**

**A) Metatitanic Acid (in form of an aqueous suspension)**

Metatitanic Acid was provided as a commercial product (in suspension form). The content of TiO$_2$ was adjusted to a calculated TiO$_2$ content of 29% by addition of water. This suspension was used in the procedures of examples 1 to 9.

**Metal Vanadates (in the form of a powder)**

ErV$_4$ was prepared according to the description [0018] disclosed in EP 1682266.
FeV₄ was prepared according to the description disclosed in US 8,465,713 column 18, line 31-65.

Fe₂Al₂V₄ was prepared according to a description as disclosed in WO2011/127505 page 17 for compound 8, with the exception that the stoichiometric ratio of Fe-Nitrate and Al-Nitrate was calculated for a final compound of Fe₂Al₂V₄ instead of Fe₂Al₂V₄.

Example 1

Preparation of a catalyst composition TiO₂/WO₃/ErV₄ (81.6/10/8.4, weight parts) using MTA, Ammonium metatungstate (AMT) and ErV₄

139.3 g of a suspension of metatitanic acid (TiO₂ content 29 %) was put into a glass beaker and diluted with 200 ml of deionized water. 5.48 g of ammonium metatungstate (WO₃ content 91.2%) dissolved in 15 ml of deionized water was added to the slurry obtained and the mixture obtained was stirred for 20 minutes at room temperature. To the mixture obtained 4.2 g of ErV₄, preheated at 700°C / 10 hours prior to use, was added and the mixture obtained was stirred for 20 minutes. The slurry obtained was heated to 90°C and the excess of water was evaporated. The mixture obtained was dried at 100°C / 16 hours and finally calcined at 600°C / 3 hours.

50 g of TiO₂/WO₃/ErV₄ (81.6/10/8.4) was obtained.

The catalyst composition was characterized by XRD analysis. The presence of anatase as a major TiO₂ phase and ErV₄ as the vanadate constituent was determined.

Example 2

Preparation of catalyst composition TiO₂/WO₃/ErV₄ (81.6/10/8.4, weight parts) using MTA, Ammonium paratungstate (APT) and ErV₄

Example 2 was carried out according to the method of example 1 with the difference that instead of ammonium metatungstate 5.63 g of ammonium paratungstate (APT) (WO₃ content 88.9 %) was suspended in 30 ml of water, adding 10 g of monoethanolamin, the mixture being heated to 50°C to dissolve the APT.

50 g of TiO₂/WO₃/ErV₄ (81.6/10/8.4) was obtained.

The catalyst composition was characterized by XRD analysis. The presence of anatase as a major TiO₂ phase and ErV₄ as the vanadate constituent was determined.

The XRD spectra was identical with the spectrum of the compound prepared according to example 1.

Example 3

Preparation of catalyst composition TiO₂/WO₃/ErV₄ (81.6/10/8.4, weight parts) using MTA, tungsten oxide (WO₃) and ErV₄
Example 3 was carried out according to the method of example 1 with the difference that instead of ammonium metatungstate 5.04 g of tungsten oxide (WO₃ content 99.3 %) was suspended in 30 ml of water, 10 g of monoethanolamine was added and the mixture obtained was heated to 50°C to dissolve the WO₃.
50 g of TiO₂/WO₃/ErVO₄ (81.6/10/8.4) was obtained.
The catalyst composition was characterized by XRD analysis. The presence of anatase as a major TiO₂ phase and ErVO₄ as the vanadate constituent was determined. The XRD spectra was identical with the spectrum of the compound prepared according to example 1.

Example 4
Preparation of catalyst composition TiO₂/WO₃/FeVO₄ (75/10/15, weight parts) using MTA, Ammonium metatungstate (AMT) and FeVO₄
256 g of a suspension of metatitanic acid (TiO₂ content 29%) was put into a glass beaker and diluted with 200 ml of deionized water. 10.96 g of ammonium metatungstate (WO₃ content 91.2%) dissolved in 30 ml of deionized water was added to the slurry and the mixture obtained was stirred for 20 minutes at room temperature. To the mixture obtained 15 g of FeVO₄, preheated at 630°C / 20 hours prior to use, was added and the mixture obtained was stirred for 20 minutes. The slurry obtained was heated up to 90°C and the excess of water was evaporated. The mixture obtained was dried at 100°C / 16 hours and finally split into 2 parts, one part was calcined at 450°C / 3 hours and the second part was calcined at 600°C / 3 hours.
50 g of TiO₂/WO₃/FeVO₄ (75/10/15) out of each calcination was obtained.
Both catalyst compositions were characterized by XRD analysis. The XRD of the catalyst composition made at 450°C / 3 hours indicated the presence of TiO₂ in the anatase form only but no crystalline vanadate constituent.
The XRD of the catalyst composition made at 600°C / 3 hours indicated TiO₂ being present in anatase and rutile form in a ratio of approximately 1:1 and in addition peaks corresponding to FeVO₄ and an additional Fe-V phase.

Example 5
Preparation of catalyst composition TiO₂/WO₃/Fe₀.₅Al₀.₅VO₄ (75/10/15, weight parts) using MTA, Ammonium metatungstate (AMT) and Fe₀.₅Al₀.₅VO₄
128 g of a suspension of metatitanic acid (TiO₂ content 29%) was put into a glass beaker and diluted with 200 ml of deionized water. 5.48 g of ammonium metatungstate (WO₃ content 91.2%) dissolved in 15 ml of deionized water was added to the slurry and the mixture obtained was stirred for 20 minutes at room temperature. To the mixture obtained 7.5 g of Fe₀.₅Al₀.₅VO₄, preheated at 550°C / 10 hours prior to use, was added and the mixture
obtained was stirred for 20 minutes. The slurry obtained was heated up to 90°C and the excess of water was evaporated. The mixture obtained was dried at 100°C / 16 hours and finally calcined at 600°C / 3 hours. 50 g of Ti0₂/WO₃/Fe₉Al₉V₂O₄ (75/10/15) was obtained. The catalyst composition was characterized by XRD analysis indicating the presence of anatase as TiO₂ phase only which indicates a higher thermal stability of the catalyst composition in comparison to that of example 4 in which FeV0₄ was used.

Example 6
Preparation of catalyst composition Ti0₂/WO₃/ErV0₄/V₂O₅ (79.6/10/8.4/2, weight parts) using MTA, Ammonium metatungstate (AMT), ErV0₄ and Ammonium metavanadate (AMV)
To 271.67 g of a suspension of metatitanic acid (TiO₂ content 29.3%) was added a solution of 10.96 g of ammonium metatungstate (WO₃ content 91.2%) in 30 ml of deionized water and the mixture obtained was stirred for 20 minutes at room temperature. To the mixture obtained 8.4 g of ErV0₄ preheated at 700°C / 10 hours, was added and the suspension obtained was stirred for 20 minutes. 2.57 g of ammonium metavanadate (V₂O₅ content 77.84%) was dissolved in 200 ml of 80°C hot deionized water and then poured into the above mixture and the mixture obtained was stirred vigorously for 15 minutes. The slurry obtained was heated up to 90°C and excess of water was evaporated. The mixture obtained was dried at 100°C / 16 hours and finally split into two parts: one part was calcined at 450°C / 3 hours and the second part was calcined at 600°C / 3 hours. 50 g of Ti0₂/WO₃/ErV0₄/V₂O₅ (79.6/10/8.4/2) from each calcination were obtained. Both catalyst compositions were characterized by XRD analysis. The XRD of both catalyst composition produced indicated the presence of TiO₂ in the anatase form only and crystalline ErV0₄.

Example 7
Preparation of catalyst composition Ti0₂/WO₃/Si0₂/ErV0₄ (71.6/10/10/8.4, weight parts) using MTA, Ammonium metatungstate (AMT), Tetraethyl orthosilicate (a product from Sigma Aldrich) and ErV0₄
To 244.3 g of a suspension of metatitanic acid (TiO₂ content 29.3%) was added a solution of 10.96 g of ammonium metatungstate (WO₃ content 91.2%) in 30 ml of deionized water and the mixture obtained was stirred for 20 minutes at room temperature. To the mixture obtained 8.4 g of ErV0₄ preheated at 700°C / 10 hours, was added and the suspension obtained was stirred for 5 minutes. 34.7 g of tetraethyl orthosilicate (SiO₂ content 28.8%) was then poured into the above mixture and the mixture obtained was stirred vigorously for 15
minutes. The slurry obtained was heated up to 90°C and excess of water was evaporated. The mixture obtained was dried at 100°C / 16 hours and calcined at 600°C / 3 hours. 100 g of TiO₂/WO₃/SiO₂/ErV₀₄ (71.6/10/10/8.4) was obtained.
The catalyst composition was characterized by XRD analysis indicating the presence of anatase as a major TiO₂ phase and ErV₀₄ as the vanadate constituent.

Example 8
Preparation of catalyst composition TiO₂/WO₃/CeO₂/ErV₀₄ (71.6/10/10/8.4, weight parts) using MTA, Ammonium metatungstate (AMT), Cerium acetate and ErV₀₄
To 244.3 g of a suspension of metatitanic acid (TiO₂ content 29.3%) was added a solution of 10.96 g of ammonium metatungstate (WO₃ content 91.2%) in 30 ml of deionized water and the mixture obtained was stirred for 20 minutes at room temperature. To the mixture obtained 8.4 g of ErV₀₄ preheated at 700°C / 10 hours, was added and the suspension obtained was stirred for 5 minutes. 20.5 g of cerium acetate (CeO₂ content 48.8%) was dissolved in 150 ml of deionized water and the solution obtained was poured into the above mixture. The mixture obtained was stirred vigorously for 15 minutes. The slurry obtained was heated up to 90°C and excess of water was evaporated. The mixture obtained was dried at 100°C / 16 hours and calcined at 600°C / 3 hours. 100g of TiO₂/WO₃/CeO₂/ErV₀₄ (71.6/10/10/8.4) was obtained. The catalyst composition was characterized by XRD analysis indicating the presence of anatase as a TiO₂ phase only and ErV₀₄ as the vanadate constituent.

Example 9
Preparation of catalyst composition TiO₂/WO₃/ZrO₂/ErV₀₄ (71.6/10/10/8.4, weight parts) using MTA, Ammonium metatungstate (AMT), Zirconium acetate and ErV₀₄
To 244.3 g of a suspension of metatitanic acid (TiO₂ content 29.3%) was added a solution of 10.96 g of ammonium metatungstate (WO₃ content 91.2%) in 30 ml of deionized water and the mixture obtained was stirred for 20 minutes at room temperature. To the mixture obtained 8.4 g of ErV₀₄ preheated at 700°C / 10 hours, was added and the suspension obtained was stirred for 5 minutes. 33.3 g of Zirconium acetate (ZrO₂ content 30%) was dissolved in 50 ml of deionized water and the solution obtained was poured into the above mixture. The mixture obtained was stirred vigorously for 15 minutes. The slurry obtained was heated up to 90°C and excess of water was evaporated. The mixture obtained was dried at 100°C / 16 hours and calcined at 600°C / 3 hours. 100 g of TiO₂/WO₃/ZrO₂/ErV₀₄ (71.6/10/10/8.4) was obtained. The catalyst composition was characterized by XRD analysis indicating the presence of anatase as a TiO₂ phase only and ErV₀₄ as the vanadate constituent.
Example 10

Determination of catalytic activity of TiC^/W05/SiC V ErVCV (71.6/10/10/8.4/) prepared according to example 7 and TiO2/WO5/Si(V ErVO4 (71.6/10/10/8.4/) prepared according to comparative example 1

Conditions for catalytic testing:

Sample preparation

Powders yielded by the process according to example 1 of the invention and yielded by the process as described in comparative example 1 were pressed into pellets, crushed and sieved in the range 355-425 µm.

Determination of catalytic activity

The test was carried out in a microreactor as described in WO 2010/121280 A1. As a model feed gas for NOx component there was used NO only. More in detail the feed consisted of NH3/N2, NO/N2, O2, N2. Mass flow meters were used to measure and control the single gaseous stream while an injection pump was used to introduce water. The feed stream was preheated and premixed and ammonia was added to the gaseous mixture immediately before entering the reactor to avoid side reactions. A tubular quartz reactor was employed inserted in a furnace. Temperature was controlled by a thermocouple inserted in the catalyst bed. Activity of the catalysts was determined under stationary conditions in a temperature range of 200°C to 500°C. Gas composition analysis was carried out with an FT-IR spectrometer (MKS Multigas Analyzer 2030) equipped with a heated multi-pass gas cell (5.1 lm).

Table 1: Reaction conditions and gas composition for catalytic test A

<table>
<thead>
<tr>
<th>Catalyst weight</th>
<th>100.0 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>350-425 µm</td>
</tr>
<tr>
<td>Total flow</td>
<td>0.3 l/min</td>
</tr>
<tr>
<td>Space velocity</td>
<td>180000 h⁻¹</td>
</tr>
<tr>
<td>Temperature</td>
<td>200-500°C</td>
</tr>
<tr>
<td>NO cone.</td>
<td>200 ppm</td>
</tr>
<tr>
<td>NH3 cone.</td>
<td>220 ppm</td>
</tr>
<tr>
<td>O2 cone.</td>
<td>20000 ppm</td>
</tr>
<tr>
<td>H2O cone.</td>
<td>10%</td>
</tr>
<tr>
<td>N2 cone.</td>
<td>balance</td>
</tr>
</tbody>
</table>
Determined NOx conversion are shown in the following table 2.

Table 2: Determined NOx conversion in % of Ti0₂/W0₃/Si0₂/ErV0₄ (71.6/10/10/8.4/) prepared according to example 7 (Ex 7 = compound of example 7) and prepared according to comparative example 1 (Comp Ex 1 = compound of comparative example 1).

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<th>Temp. °C</th>
<th>200</th>
<th>230</th>
<th>250</th>
<th>270</th>
<th>300</th>
<th>320</th>
<th>350</th>
<th>380</th>
<th>420</th>
<th>450</th>
<th>480</th>
<th>500</th>
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<td>10</td>
<td>26</td>
<td>42</td>
<td>59</td>
<td>76</td>
<td>84</td>
<td>90</td>
<td>91</td>
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<td>87</td>
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<td>80</td>
</tr>
<tr>
<td>Comp Ex 1</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>7</td>
<td>15</td>
<td>23</td>
<td>37</td>
<td>49</td>
<td>58</td>
<td>60</td>
<td>60</td>
<td>59</td>
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</tbody>
</table>

Comparative example 1

Preparation of catalyst composition Ti0₂/W0₃/Si0₂/ErV0₄ (73.2/9.2/9.2/8.4, weight parts) similar to a process known from prior art (see US 8,465,713, comp. example 2)

91.6 g of Ti0₂/W0₃/Si0₂ known as a commercial product CristalACTiV™ DT-58 was suspended in 350 mL DI water and stirred for 15 minutes. 8.4g of ErV0₄ was added to the suspension and the mixture obtained was again stirred for 15 minutes at room temperature. Excess of water was then evaporated and the slurry was brought to dryness under continuous stirring at 80 to 100°C. Finally the mixture was dried overnight at 110°C and then calcined at 600°C / 3 hours.
Patent Claims

1. A process for the preparation of a titania/metal vanadate based catalyst composition, comprising the steps of bringing into contact an amount of metatitanic acid which is sufficient to yield an amount of 60 wt.% to 99 wt.% of titania in the composition with an amount of one or more metal vanadates of the general formula

   \[ \text{MeVan} \quad (I) \]

   which is sufficient to yield an amount of 0.1 wt.% to 25 wt.% of MeVan in the composition,

   wherein Me denotes Mg, Ca, Sr, Ba, Zr, Mn, Fe, Cu, Ag, Al, Bi, Sb, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Yb, or individual mixtures thereof, and Van denotes \( V_2O_7^{3-}, V_2O_7^{4+} \) or mixtures thereof, to form an intimate mixture, and calcining the mixture obtained.

2. A process according to claim 1, comprising
   a) providing metatitanic acid in dried form or in suspended form in a liquid,
   b) adding the metal vanadate of general formula I as defined in claim 1,
   c) forming an intimate mixture of the compounds of a) and b),
   d) removing the suspension liquid from the mixture of c), if present, and
   e) calcining the resulting solid.

3. A process according to any one of claims 1 to 2, wherein Me denotes Al, Fe, Zr, Ce, Pr, Nd, Gd, Dy or Er, in particular Al, Fe, Ce, Gd, Dy or Er, or individual mixtures thereof.

4. A process according to any one of claims 2 to 3, wherein additionally ammonium metavanadate and/or ammonium polyvanadate is added before step e), in particular after step b), preferably before step c).

5. A process according to any one of claims 2 to 4, wherein additionally one or more metal oxides or precursors thereof and/or a silicium compound, particularly \( \text{SiO}_2 \) or a precursor thereof, are added.

6. A process according to claim 5, wherein before step e) additionally are added
   A) a metal oxide, in particular an oxide of Mg, Ca, Sr, Ba, Zr, Mn, Fe, Cu, Ag, Al, Bi, Sb, W, Mo, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Yb,
   B) \( \text{SiO}_2 \),
CI) individual mixtures of one or more oxides indicated under Al) and Bl), wherein the metal oxides and/or SiO₂ may be added in the form of precursors thereof.

7. A process according to any one of claims 5 or 6, wherein the precursors of metal oxides are selected from metal-carbonates, -acetates, -sulphates, -nitrates, -hydroxides, -chlorides or metal salts of any organic acid, and in case of tungsten from ammonium metatungstate or ammonium paratungstate.

8. A process according to any one of claims 5 to 7, wherein tungsten oxide or the precursor thereof is added before step b).

9. A process according to any one of claims 5 to 8, wherein oxides of metals other than tungsten, SiO₂ or precursors of said metal oxides or said SiO₂ are added after step b), preferably before step c)

10. A process according to any one of claims 4 to 9, comprising
   - contacting metatitanic acid with a tungsten compound, in particular WO₃, or a precursor thereof, such as ammonium metatungstate or ammonium paratungstate, in the presence of SiO₂ or a silicium compound which forms SiO₂ after heat treatment, or
   - in the absence of SiO₂ or a silicium compound which forms SiO₂ after heat treatment,
   - adding the metal vanadate of formula I and forming an intimate mixture.

11. A process according to any one of claims 4 to 10, wherein the amount of tungsten compound, calculated as WO₃, in weight % based on the total weight of the catalyst composition prepared, is in the range from 1% to 30% by weight, preferably 3% to 15% by weight, especially preferable 5% to 10% by weight.

12. A process according to any one of claims 4 to 11, wherein the amount of silicium compound, calculated as SiO₂, in weight % based on the total weight of the catalyst composition prepared, is in the range from 0% to 30% by weight, preferably 1 wt.% to 30 wt.%

13. A process according to any of the preceding claims, wherein the amount of metatitanic acid is sufficient to yield an amount of 60 wt.% to 95 wt.%, preferably 65 wt.% to 90 wt.%, most preferably 70 wt.% to 85 wt.% of titania in the composition.
14. A process according to any of the preceding claims, wherein the amount of MeVan is sufficient to yield an amount of 0.5 wt.% - 15 wt.% of MeVan in the composition.

15. A process according to claim 4, wherein the amount of ammonium metavanadate and/or ammonium polyvanadate is sufficient to yield an amount of 0.3 wt% to 10 wt% calculated as $V_2O_5$ in the composition.

16. A process according to any one of claims 5 to 15, wherein a metal oxide or precursor thereof is added, wherein the metal is selected from the group consisting of Cu, Mn and rare earth metals, and wherein the metal oxide or precursor thereof is added in an amount which is sufficient to yield 1 wt.% to 15 wt.% of the metal oxide in the composition.

17. A process according to any of the preceding claims for the manufacture of a composition which comprises per 100 weight parts
- 65 to 85 weight parts of TiO$_2$,
- 5 to 15 weight parts of WO$_3$,
- 5 to 20 weight parts of one or more metal vanadates, in particular selected from ErV$_2$O$_5$, FeV$_2$O$_4$, Fe$_{0.5}$Al$_{0.5}$V$_2$O$_4$, Fe$_{0.5}$Er$_{0.5}$V$_2$O$_4$,
- 0 to 15 weight parts of a metal oxide particularly selected from CeO$_2$, ZrO$_2$, V$_2$O$_5$, and -0 to 15 weight parts of SiO$_2$.

18. A process according to claim 17 for the manufacture of a composition selected from
- TiO$_2$/WO$_3$/ErV$_2$O$_5$ (81.6/10/8.4, weight parts),
- TiO$_2$/WO$_3$/FeV$_2$O$_4$ (75/10/15, weight parts),
- TiO$_2$/WO$_3$/Fe$_{0.5}$Al$_{0.5}$V$_2$O$_4$ (75/10/15, weight parts),
- TiO$_2$/WO$_3$/ErV$_2$O$_5$ (79.6/10/8.4/2, weight parts),
- TiO$_2$/WO$_3$/SiO$_2$/ErV$_2$O$_5$ (71.6/10/10/8.4, weight parts),
- TiO$_2$/WO$_3$/CeO$_2$/ErV$_2$O$_5$ (71.6/10/10/8.4, weight parts), and
- TiO$_2$/WO$_3$/ZrO$_2$/ErV$_2$O$_5$ (71.6/10/10/8.4, weight parts).

19. The use of metatitanic acid for the preparation of a titania/metal vanadate based catalyst in an one pot reaction.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J37/03 B01J37/04 B01J37/08 B01J23/847 B01J21/06
B01J23/00 B01D53/94

ADD.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J B01D

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

Electronic database consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>wo 2010/121280 AI (TREIBACHER IND AG [AT]; SCHERMANZ KARL [AT]; SAGAR AMOD [AT]; TROVAREL) 28 October 2010 (2010-10-28) cited in the application on examples 1, la, lb, ld, le, 6b, 6d examples comp 2, comp 2d, comp 2f, 16 tables claims 1, 2, 3, 4, 6, 9</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search
4 August 2016

Date of mailing of the international search report
12/08/2016

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Hol zwarth, Arnold

Form PCT/ISA/210 (second sheet) (April 2005)

page 1 of 2
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<td>CN 103 894 184 A (CHANGYI KATE NEW MATERIALS co LTD) 2 July 2014 (2014-07-02)</td>
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