

Description

The present invention relates to a process of preparing a bimetallic catalyst for the reduction of nitrogen oxides, which catalyst includes an inorganic carrier, titanium and vanadium.

5 British patent No. 1 430 730 discloses a process of preparing a catalyst for the reduction of nitrogen oxides, which process comprises applying a titanium compound and a vanadium compound to an inorganic carrier; drying the carrier; and subjecting the carrier to a heat treatment at a temperature between 200°C and 800°C in air.

It is an object of the invention to provide an improved catalyst having a higher activity.

10 To this end the process of preparing a bimetallic catalyst according to the invention is characterized in that at least one additive is applied to the inorganic carrier simultaneously with or after applying the titanium compound, which additive is selected from the group consisting of a bromine compound, a fluorine compound and an iodine compound, and in that the vanadium compound is applied to the inorganic carrier simultaneously with or after applying the additive.

15 It was found that by applying the additive or additives simultaneously with or after applying the titanium compound and by applying the vanadium compound simultaneously with or after applying the additive or additives a catalyst having an improved activity can be prepared.

It is assumed that the activity is improved because the additive improves the dispersion of the metals on the catalyst or because the additive is a promoter. It was found that a bromine compound or an iodine 20 compound has a beneficial effect on the dispersion of the metals, in particular on the dispersion of vanadium, and that a fluorine acts as a promoter.

Reference is made to US patent No. 4 394 252, which publication discloses a catalyst used in reforming a gasoline feed (which is modifying the molecules of straight-run gasoline fractions in order to improve the anti-knock quality). The catalyst comprises titanium and/or vanadium component(s) on a coke-containing 25 carrier. This publication is not relevant to the invention because a) the publication does not relate to reduction of nitrogen oxides b) the publication does not disclose an inorganic carrier and c) the disclosed heat treatment is done in a reducing environment.

Further reference is made to German Offenlegungsschrift No. 35 31 871 relating to a denoxing catalyst which is prepared by mixing clay to a titanium-containing paste which also contains vanadium and forming 30 a honeycomb from the mixture. The honeycomb is dried and calcined in air. This publication is not relevant to the present invention as the publication does not relate to impregnating an inorganic carrier with a titanium and bromine compound.

In a suitable embodiment the carrier is first contacted with a solution containing a titanium compound, and subsequently with an acidic solution containing the additive(s) and a vanadium compound. The pH of 35 the acidic solution used may be less than 5, and suitably less than 4.

In a further suitable embodiment the carrier is first contacted with an acidic solution containing a titanium compound and the additive(s), and subsequently with a solution containing a vanadium compound. The pH of the acidic solution used may be less than 5, and suitably less than 4.

In a further suitable embodiment the carrier is contacted with an acidic solution containing a titanium 40 compound, the additive(s) and a vanadium compound. The pH of the acidic solution used may be less than 5, and suitably less than 4.

The titanium compound used may suitably be a titanium halide, an organic titanium salt or an ortho-titanic acid.

The vanadium compound used may suitably be selected from the group vanadyl chloride, vanadyl 45 bromide, vanadyl sulphate and ammonium poly vanadate.

In a very suitable embodiment the additive is a bromine compound, the bromine compound used may be hydrogen bromide or ammonium bromide.

In an alternative embodiment the additive is a fluorine compound, the fluorine compound used may be hydrogen fluoride or ammonium fluoride.

50 The catalyst prepared according to the process according to the invention may be used for the reduction of nitrogen oxides, such as NO and NO₂ in the presence of NH₃. This reduction process comprises contacting a gaseous mixture containing nitrogen oxides at atmospheric pressure, at temperatures between 150°C and 350°C and at a gas hourly space velocity between 4 000 Nm³/m³/hour and 10 000 Nm³/m³/hour (1 Nm³ gas equals 1 m³ at 20°C and 0.1 MPa), wherein the molar ratio of NH₃ to nitrogen oxides is slightly below the stoichiometrically required ratio.

A suitable gaseous mixture containing NO and NO₂ which can be treated with the process according to the invention is dry gas obtained from a catalytic cracking unit.

The invention further relates to a catalyst for the reduction of nitrogen oxides prepared in the manner as described above comprising an inorganic carrier, 2—15% by mass of titanium, 1—1 500 ppm (parts per 60 million by mass) bromine and 2—15% by mass vanadium.

The invention also relates to a catalyst for the reduction of nitrogen oxides prepared in the manner as described above comprising an inorganic carrier, 2—15% by mass of titanium, 0.5—5% by mass fluorine and 2—15% by mass vanadium.

Suitable inorganic carriers are refractory materials, such as silicon oxide or aluminum oxide or 65 mixtures thereof.

The invention will now be elucidated in more detail with reference to the examples.

Unless otherwise specified, the silicon oxide carriers are carriers (ex Shell) having a particle diameter of 1.5 mm, a pore volume H_2O of about 0.9 ml/g and a specific area of 260 m^2/g . The acidic solution of $TiCl_4/H_2O$ used is manufactured by Tilcom and contains 9.2% by mass of titanium, the pH of the solution is 0 and its density is 1.33 g/ml.

The specific area of the carriers and of the catalyst samples has been determined using the BET method, and the metal dispersion has been determined using X-ray photo electron spectroscopy (XPS).

Example 1

Catalyst sample 1 was prepared according to the invention as follows. In a container 10.35 g ammonium poly vanadate was added to 57.17 g of an acidic solution of $TiCl_4/H_2O$ at a temperature between 50°C and 58°C, after 2 hours the ammonium poly vanadate was completely dissolved and the colour of the solution was dark brown. Heating was stopped. Subsequently 20 ml of an aqueous solution containing 4.45 g HBr was added at a temperature of about 48°C. The obtained solution was further diluted to 80 ml with an aqueous solution containing 18% by mass of hydrogen chloride. The obtained impregnating solution had a green colour and it was stable.

Thereupon 85 g of silicon oxide carrier was contacted with 77 ml of the impregnating solution. The colour of the carrier was black. The carrier was rotated for 1 hour, dried while being rotated for 1.5 hour, and heated in air by increasing the temperature to 120°C in 1 hour followed by maintaining the temperature at 120°C for 8 hours, raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C. After this treatment the colour of catalyst sample 1 was green.

Data pertaining to catalyst sample 1 have been included in Table 1.

Example 2

Catalyst sample 2 was prepared according to the invention as follows. In a container 10.35 g ammonium poly vanadate was added to 57.17 g of an acidic solution of $TiCl_4/H_2O$ and 15 ml of an aqueous solution containing 30% by mass of HCl at a temperature of 22°C. In 10 minutes the temperature was raised to 30°C, and during 30 minutes the temperature was maintained between 30°C and 35°C until everything dissolved. To this solution was slowly added 10 ml of an aqueous solution containing 2.62 g NH_4Br . In this way 72 ml of a solution having a green brown colour was obtained. The obtained solution was further diluted to 78 ml with water. The obtained impregnating solution was stable.

Thereupon 85 g of silicon oxide carrier was contacted with 78 ml of the impregnating solution. The colour of the carrier was black. The carrier was dried while being rotated for 2 hours, and heated in air by increasing the temperature to 120°C in 1 hour followed by maintaining the temperature at 120°C for 8 hours, raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C. After this treatment the colour of catalyst sample 2 was brown green.

Data pertaining to catalyst sample 2 have been included in Table 1.

Example 3

Catalyst sample 3 was prepared according to the invention as follows. At first 85 g of silicon oxide carrier was contacted with 78 ml of an aqueous impregnating solution containing 50.43 g of an acidic $TiCl_4/H_2O$ solution. The carrier was rotated for 1 hour, dried while being rotated for 1.5 hour, and heated in air by increasing the temperature to 120°C in 1 hour followed by maintaining the temperature at 120°C for 8 hours, raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C.

Subsequently an impregnating solution was prepared by adding 20.0 g oxalic acid slowly at a temperature between 40°C and 80°C to an aqueous solution containing 9.39 g ammonium poly vanadate dissolved in 40 ml water. At a temperature of 50°C a solution of 2.34 g NH_4Br in 10 ml water was added, and 74 ml of impregnating solution was obtained, which solution was clear and had a blue colour.

With 72 ml of this impregnation solution 85 g of the titanium coated carrier was contacted. The carrier was rotated for 1 hour, dried while being rotated for 2 hours, and heated in air by increasing the temperature to 120°C in 1 hour followed by maintaining the temperature at 120°C for 8 hours, raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C. After this treatment the colour of catalyst sample 3 was light brown.

Data pertaining to catalyst sample 3 have been included in Table 1.

Example 4

Catalyst sample 4 was prepared according to the invention as follows. At first 85 g of silicon oxide carrier was contacted with 152 ml of an aqueous impregnating solution containing a titanium compound and a bromine compound. The impregnating solution was prepared as follows. In a container 27.67 g of an aqueous solution containing 25% by mass NH_4OH was added at a temperature between 40°C and 80°C to 103.04 g of an acidic $TiCl_4/H_2O$ solution. Subsequently 10 ml water was added, and at a temperature of 50°C 4.64 g NH_4Br dissolved in 8 ml water was added. No bromine escaped. Water was added to obtain a volume of 156 ml. Thereupon 85 g of silicon oxide carrier was contacted with 152 ml of this impregnating solution. The carrier was rotated for 1 hour, dried while being rotated for 2 hours, and heated in air by increasing the temperature to 120°C in 1 hour followed by maintaining the temperature at 120°C for 8 hours, raising the

EP 0 256 590 B1

temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C.

Subsequently an impregnating solution was prepared by adding 19.03 g oxalic acid slowly at a temperature between 40°C and 80°C to an aqueous solution containing 9.19 g ammonium poly vanadate dissolved in 50 ml water. A volume of 77 ml of impregnating solution was obtained, which solution was clear and had a blue colour.

With 68 ml of this impregnation solution 85 g of the titanium coated carrier was contacted. The carrier was rotated for 1 hour, dried while being rotated for 2 hours, and heated in air by increasing the temperature to 120°C in 1 hour followed by maintaining the temperature at 120°C for 8 hours, raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C. After this treatment the colour of catalyst sample 4 was light brown yellow.

Data pertaining to catalyst sample 4 have been included in Table 1.

TABLE 1

catalyst sample	specific area m ₂ /g	mass content			XPS atomic ratio	
		%Ti	%V	ppm Br	Ti/Si	V/Si
1	220	5.22	5.25	12	0.023	0.031
2	198	4.88	5.08	<100	0.016	0.028
3	—	4.66	4.20	24	0.009	0.045
4	166	4.34	3.66	114	0.003	0.039

In Table 1 "—" denotes that a value has not been determined.

Example 5

Catalyst sample 5 was prepared according to the invention as follows. In a container 10.35 g ammonium poly vanadate was mixed with 57.17 g of an acidic solution of TiCl₄/H₂O and 15 ml of an aqueous solution containing 30% by mass of hydrogen chloride. After stirring for 30 minutes at a temperature between 30°C and 35°C, all components were completely dissolved. Heating was stopped. Subsequently 9 ml of an aqueous solution containing 4.11 g NH₄F was added.

Thereupon 85 g of silicon oxide carrier was contacted with 77 ml of the impregnating solution. The carrier was rotated for 1 hour, dried while being rotated for 2 hours, and heated in air by increasing the temperature to 120°C in 1 hour followed by maintaining the temperature at 120°C for 8 hours, raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C. After this treatment the colour of catalyst sample 5 was green brown. The catalyst sample 5 contained 5.13% by mass titanium, 5.35% by mass vanadium and 2.00% by mass fluorine, and its specific area was 147 m²/g.

Example 6

To study the activity of catalyst samples 1 and 5 for the reduction of nitrogen oxide in the presence of NH₃, a sample thereof was arranged in a reactor having a volume of 60 ml and a gaseous mixture having a predetermined temperature was supplied to the reactor at a predetermined rate. The composition of the effluents leaving the reactor was determined with a Thermo Electron model 10A analyser.

The composition of the gaseous mixture used was 5% by volume O₂, 13% by volume CO₂, 6% by volume H₂O, 400 ppmv (parts per million by volume) NO, and 600 ppmv NH₃, the remainder being nitrogen.

The gaseous mixture was supplied to the reactor at atmospheric pressure and at such rates that the gas hourly space velocity was 4 000 Nm³/m³/hour and 10 000 Nm³/m³/hour, wherein 1 Nm³ gas equals 1 m³ at 20°C and 0.1 MPa.

The conversion is defined as the ratio of the difference of the NO concentrations in the gaseous mixture and in the effluent to the NO concentration in the gaseous mixture.

For catalyst sample 1 the conversion at a gas hourly space velocity of 4 000 Nm³/m³/hour and at a temperature of 150°C was 92%, and at a temperature of 200°C more than 99.5%, and the conversion at a gas hourly space velocity of 10 000 Nm³/m³/hour and at a temperature of 150°C was 64%, and at a temperature of 200°C 94%.

For catalyst sample 5 the conversion at a gas hourly space velocity of 4 000 Nm³/m³/hour and at a temperature of 150°C was 84%, and at a temperature of 200°C 99%.

Comparative Example

A titanium and vanadium containing catalyst was prepared as follows. At first 700 g of silicon oxide carrier was contacted with an impregnating solution containing 361 ml TiCl₄/H₂O and 424 ml H₂O and the

carrier was rotated for 1 hour. Subsequently the carrier was dried while being rotated for 2.5 hours, and then dried at 120°C for 2 hours, and thermally treated by raising the temperature to 450°C in 1 hour. Subsequently 85 g of the treated carrier was contacted with 69.5 ml of an aqueous solution containing 8.78 g ammonium poly vanadate and 21 g $\text{H}_2\text{C}_2\text{O}_4$ and the carrier was rotated for 1 hour. Subsequently the carrier was dried while being rotated for 1.5 hours, dried at 120°C for 8 hours, and thermally treated by raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C. The catalyst sample contained 5.10% by mass titanium and 4.86% by mass vanadium, and its specific area was 194 m^2/g .

The gaseous mixture of Example 6 was contacted under the conditions of Example 6 with this catalyst sample. The NO conversion at a gas hourly space velocity of 4000 $\text{Nm}^3/\text{m}^3/\text{hour}$ at 150°C was 54% and at 200°C 94%.

Claims

1. Process of preparing a bimetallic catalyst for the reduction of nitrogen oxides comprising applying a titanium compound and a vanadium compound to an inorganic carrier; drying the carrier; and subjecting the carrier to a heat treatment at a temperature between 200°C and 800°C in air, characterized in that at least one additive is applied to the inorganic carrier simultaneously with or after applying the titanium compound, which additive is selected from the group consisting of a bromine compound, a fluorine compound and an iodine compound, and in that the vanadium compound is applied to the inorganic carrier simultaneously with or after applying the additive.
2. Process as claimed in claim 1, wherein the carrier is first contacted with a solution containing a titanium compound, and subsequently with an acidic solution containing the additive(s) and a vanadium compound.
3. Process as claimed in claim 1, wherein the carrier is first contacted with an acidic solution containing a titanium compound and the additive(s), and subsequently with a solution containing a vanadium compound.
4. Process as claimed in claim 1, wherein the carrier is contacted with an acidic solution containing a titanium compound, the additive(s) and a vanadium compound.
5. Process as claimed in any one of the claims 2—4, wherein the pH of the acidic solution is less than 5.
6. Process as claimed in any one of the claims 1—5, wherein the titanium compound used is a titanium halide, an organic titanium salt or an ortho-titanic acid.
7. Process as claimed in any one of the claims 1—6, wherein the vanadium compound used is selected from the group vanadyl chloride, vanadyl bromide, vanadyl sulphate and ammonium poly vanadate.
8. Process as claimed in any one of the claims 1—7, wherein the additive is a bromine compound.
9. Process as claimed in claim 8, wherein the bromine compound used is hydrogen bromide or ammonium bromide.
10. Process as claimed in any one of the claims 1—7, wherein the additive is a fluorine compound.
11. Process as claimed in claim 10, wherein the fluorine compound used is hydrogen fluoride or ammonium fluoride.
12. Catalyst for the reduction of nitrogen oxides prepared according to the process as claimed in any one of the claims 1—9 comprising an inorganic carrier, 2—15% by mass of titanium, 1—1 500 ppm bromine and 2—15% by mass vanadium.
13. Catalyst for the reduction of nitrogen oxides prepared according to the process as claimed in any one of the claims 1—7 or 10 or 11 comprising an inorganic carrier, 2—15% by mass of titanium, 0.5—5% by mass fluorine and 2—15% by mass vanadium.

Patentansprüche

1. Verfahren zur Herstellung eines bimetalischen Katalysators für die Reduktion von Stickoxiden, welches ein Aufbringen einer Titanverbindung und einer Vanadiumverbindung auf einen anorganischen Träger; ein Trocknen des Trägers; und das Ausführen einer Wärmebehandlung des Trägers bei einer Temperatur zwischen 200°C und 800°C in Luft umfaßt, dadurch gekennzeichnet, daß wenigstens ein Additiv gleichzeitig mit oder nach dem Aufbringen der Titanverbindung auf den anorganischen Träger aufgebracht wird, welches Additiv aus der aus einer Bromverbindung, einer Fluorverbindung und einer Iodverbindung bestehenden Gruppe ausgewählt wird, und daß die Vanadiumverbindung gleichzeitig mit oder nach dem Aufbringen des Additivs auf den anorganischen Träger aufgebracht wird.
2. Verfahren nach Anspruch 1, worin der Träger zunächst mit einer eine Titanverbindung enthaltenden Lösung und hierauf mit einer sauren Lösung in Kontakt gebracht wird, die das oder die Additive und eine Vanadiumverbindung enthält.
3. Verfahren nach Anspruch 1, worin der Träger zunächst mit einer sauren, eine Titanverbindung und das oder die Additive enthaltenden Lösung und anschließend mit einer eine Vanadiumverbindung enthaltenden Lösung in Kontakt gebracht wird.
4. Verfahren nach Anspruch 1, worin der Träger mit einer sauren Lösung in Kontakt gebracht wird, die eine Titanverbindung, das oder die Additive und eine Vanadiumverbindung enthält.



carrier was rotated for 1 hour. Subsequently the carrier was dried while being rotated for 2.5 hours, and then dried at 120°C for 2 hours, and thermally treated by raising the temperature to 450°C in 1 hour. Subsequently 85 g of the treated carrier was contacted with 69.5 ml of an aqueous solution containing 8.78 g ammonium poly vanadate and 21 g H₂C₂O₄, and the carrier was rotated for 1 hour. Subsequently the carrier was dried while being rotated for 1.5 hours, dried at 120°C for 8 hours, and thermally treated by raising the temperature to 450°C in 1 hour and maintaining the temperature for 1 hour at 450°C. The catalyst sample contained 5.10% by mass titanium and 4.86% by mass vanadium, and its specific area was 194 m²/g.

The gaseous mixture of Example 6 was contacted under the conditions of Example 6 with this catalyst sample. The NO conversion at a gas hourly space velocity of 4000 Nm³/m³/hour at 150°C was 54% and at 200°C 94%.

Claims

1. Process of preparing a bimetallic catalyst for the reduction of nitrogen oxides comprising applying a titanium compound and a vanadium compound to an inorganic carrier; drying the carrier; and subjecting the carrier to a heat treatment at a temperature between 200°C and 800°C in air, characterized in that at least one additive is applied to the inorganic carrier simultaneously with or after applying the titanium compound, which additive is selected from the group consisting of a bromine compound, a fluorine compound and an iodine compound, and in that the vanadium compound is applied to the inorganic carrier simultaneously with or after applying the additive.
2. Process as claimed in claim 1, wherein the carrier is first contacted with a solution containing a titanium compound, and subsequently with an acidic solution containing the additive(s) and a vanadium compound.
3. Process as claimed in claim 1, wherein the carrier is first contacted with an acidic solution containing a titanium compound and the additive(s), and subsequently with a solution containing a vanadium compound.
4. Process as claimed in claim 1, wherein the carrier is contacted with an acidic solution containing a titanium compound, the additive(s) and a vanadium compound.
5. Process as claimed in any one of the claims 2—4, wherein the pH of the acidic solution is less than 5.
6. Process as claimed in any one of the claims 1—5, wherein the titanium compound used is a titanium halide, an organic titanium salt or an ortho-titanic acid.
7. Process as claimed in any one of the claims 1—6, wherein the vanadium compound used is selected from the group vanadyl chloride, vanadyl bromide, vanadyl sulphate and ammonium poly vanadate.
8. Process as claimed in any one of the claims 1—7, wherein the additive is a bromine compound.
9. Process as claimed in claim 8, wherein the bromine compound used is hydrogen bromide or ammonium bromide.
10. Process as claimed in any one of the claims 1—7, wherein the additive is a fluorine compound.
11. Process as claimed in claim 10, wherein the fluorine compound used is hydrogen fluoride or ammonium fluoride.
12. Catalyst for the reduction of nitrogen oxides prepared according to the process as claimed in any one of the claims 1—9 comprising an inorganic carrier, 2—15% by mass of titanium, 1—1 500 ppm bromine and 2—15% by mass vanadium.
13. Catalyst for the reduction of nitrogen oxides prepared according to the process as claimed in any one of the claims 1—7 or 10 or 11 comprising an inorganic carrier, 2—15% by mass of titanium, 0.5—5% by mass fluorine and 2—15% by mass vanadium.

Patentansprüche

1. Verfahren zur Herstellung eines bimetalischen Katalysators für die Reduktion von Stickoxiden, welches ein Aufbringen einer Titanverbindung und einer Vanadiumverbindung auf einen anorganischen Träger; ein Trocknen des Trägers; und das Ausführen einer Wärmebehandlung des Trägers bei einer Temperatur zwischen 200°C und 800°C in Luft umfaßt, dadurch gekennzeichnet, daß wenigstens ein Additiv gleichzeitig mit oder nach dem Aufbringen der Titanverbindung auf den anorganischen Träger aufgebracht wird, welches Additiv aus der aus einer Bromverbindung, einer Fluorverbindung und einer Iodverbindung bestehenden Gruppe ausgewählt wird, und daß die Vanadiumverbindung gleichzeitig mit oder nach dem Aufbringen des Additivs auf den anorganischen Träger aufgebracht wird.
2. Verfahren nach Anspruch 1, worin der Träger zunächst mit einer eine Titanverbindung enthaltenden Lösung und hierauf mit einer sauren Lösung in Kontakt gebracht wird, die das oder die Additive und eine Vanadiumverbindung enthält.
3. Verfahren nach Anspruch 1, worin der Träger zunächst mit einer sauren, eine Titanverbindung und das oder die Additive enthaltenden Lösung und anschließend mit einer eine Vanadiumverbindung enthaltenden Lösung in Kontakt gebracht wird.
4. Verfahren nach Anspruch 1, worin der Träger mit einer sauren Lösung in Kontakt gebracht wird, die eine Titanverbindung, das oder die Additive und eine Vanadiumverbindung enthält.



EP 0 256 590 B1

5. Verfahren nach einem der Ansprüche 2 bis 4, worin der pH-Wert der sauren Lösung unter 5 liegt.
6. Verfahren nach einem der Ansprüche 1 bis 5, worin die eingesetzte Titanverbindung ein Titanhalogenid, ein organisches Titansalz oder eine Orthotitansäure ist.
7. Verfahren nach einem der Ansprüche 1 bis 6, worin die eingesetzte Vanadiumverbindung aus der
5 Gruppe Vanadylchlorid, Vanadylbromid, Vanadylsulfat und Ammoniumpolyvanadat ausgewählt wird.
8. Verfahren nach einem der Ansprüche 1 bis 7, worin das Additiv eine Bromverbindung ist.
9. Verfahren nach Anspruch 8, worin die eingesetzte Bromverbindung Bromwasserstoff oder Ammoniumbromid ist.
10. Verfahren nach einem der Ansprüche 1 bis 7, worin das Additiv eine Fluorverbindung ist.
10 11. Verfahren nach Anspruch 10, worin die eingesetzte Fluorverbindung Fluorwasserstoff oder Ammoniumfluorid ist.
12. Katalysator zur Reduktion von Stickoxiden, hergestellt gemäß dem Verfahren, wie in einem der Ansprüche 1 bis 9 beansprucht, umfassend einen anorganischen Träger, 2 bis 15 Masse-% Titan, 1 bis 1,500 ppm Brom und 2 bis 15 Masse-% Vanadium.
15 13. Katalysator zur Reduktion von Stickoxiden, hergestellt gemäß dem Verfahren, wie in einem der Ansprüche 1 bis 7 oder 10 oder 11 beansprucht, umfassend einen anorganischen Träger, 2 bis 15 Masse-% Titan, 0,5 bis 5 Masse-% Fluor und 2 bis 15 Masse-% Vanadium.

Revendications

- 20 1. Procédé de préparation d'un catalyseur bimétallique pour la réduction d'oxydes d'azote, comprenant l'application d'un composé du titane et d'un composé du vanadium à un support inorganique; le séchage du support; et l'exposition du support à un traitement thermique à une température comprise entre 200°C et 800°C dans l'air, caractérisé en ce qu'au moins un additif est appliqué au support inorganique
25 simultanément avec l'application du composé du titane ou après, cet additif étant choisi dans le groupe constitué par un composé du brome, un composé du fluor et un composé de l'iode, et en ce que le composé du vanadium est appliqué au support inorganique simultanément avec l'application de l'additif ou après.
2. Procédé selon la revendication 1, dans lequel le support est mis en contact d'abord avec une solution
30 contenant un composé du titane et ensuite avec une solution acide contenant l'additif ou les additifs et un composé du vanadium.
3. Procédé selon la revendication 1, dans lequel le support est mis en contact d'abord avec une solution acide contenant un composé du titane et l'additif ou les additifs et ensuite avec une solution contenant un composé du vanadium.
35 4. Procédé selon la revendication 1, dans lequel le support est mis en contact avec une solution acide contenant un composé du titane, l'additif ou les additifs et un composé du vanadium.
5. Procédé selon l'une quelconque des revendications 2—4, dans lequel le pH de la solution acide est au-dessous de 5.
6. Procédé selon l'une quelconque des revendications 1—5, dans lequel le composé du titane utilisé est
40 un halogénure de titane, un sel organique de titane ou un acide ortho-titanique.
7. Procédé selon l'une quelconque des revendications 1—6, dans lequel le composé du vanadium utilisé est choisi dans le groupe constitué par le chlorure de vanadyle, le bromure de vanadyle, le sulfate de vanadyle et du poly vanadate d'ammonium.
8. Procédé selon l'une quelconque des revendications 1—7, dans lequel l'additif est un composé du
45 brome.
9. Procédé selon la revendication 8, dans lequel le composé du brome utilisé est du bromure d'hydrogène ou du bromure d'ammonium.
10. Procédé selon l'une quelconque des revendications 1—7, dans lequel l'additif est un composé du fluor.
50 11. Procédé selon la revendication 10, dans lequel le composé du fluor utilisé est du fluorure d'hydrogène ou du fluorure d'ammonium.
12. Catalyseur pour la réduction d'oxydes d'azote préparé par un procédé selon l'une quelconque des revendications 1—9, comprenant un support inorganique, 2—15 % en poids de titane, 1—1500 ppm de brome et 2—15 % en poids de vanadium.
55 13. Catalyseur pour la réduction d'oxydes d'azote préparé par un procédé selon l'une quelconque des revendications 1—7 ou 10 ou 11, comprenant un support inorganique, 2—15 % en poids de titane, 0,5—5 % en poids de fluor et 2—15 % en poids de vanadium.