Catalyst for Selective Reduction of Nitrogen Oxides, Method for Making Same and Use Thereof

Abstract: A catalyst for the selective catalytic reduction of a nitrogen oxide, comprising a first component selected from oxides of a transition metal other than the metal contained in the second component, or a mixture or combination thereof, a second component selected from cerium oxides, cerium-zirconium composite oxides, and cerium-titanium composite oxides, and combinations thereof. The catalyst can be utilized in pellet form, or coated onto a porous monolithic ceramic to form a honeycomb-shaped catalyst. Provided in the present invention is also the process for making said catalyst, which includes: preparing the first component from the precursor of the first component; preparing the second component; and loading the first component onto the second component.
CATALYST FOR SELECTIVE REDUCTION OF NITROGEN OXIDES, METHOD FOR MAKING SAME AND USE THEREOF

TECHNICAL FIELD

[0001] The present invention relates to a catalyst for the catalytic reduction of nitrogen oxides, method for making same and use thereof. In particular, the present invention relates to an oxide catalyst for the selective catalytic reduction of nitrogen oxides, method for making same and use thereof in reducing NO₅ emission in stationery and mobile sources. The present invention is useful, e.g., in reducing NOₓ emission from automobiles and other vehicles.

BACKGROUND

[0002] As is well known, nitrogen oxides (including NO₂, N₂O, and NO, hereafter collectively "NOₓ") are products formed from the combustion of gases in the air. At high temperature, NOₓ is more thermodynamically stable N₂ and O₂. Therefore, it is unavoidable for NOₓ to become a pollutant produced in many high-temperature processes, such as engine combustion and various industrial processes.

[0003] There are two main approaches to reducing NOₓ pollution in air: reduction of emission from the sources and post-treatment of the waste gas. In the first approach, various technologies are employed to improve combustion. In the second approach, various physical and/or chemical processes are utilized to remove NOₓ from the waste gas, including industrially accepted technologies such as selective catalytic reduction (hereafter abbreviated as "SCR") or non-selective catalytic reduction (NSCR), and new technologies such as storage-catalytic reduction systems.

[0004] For NOₓ emitted from a mobile sources (such as a diesel engine, with the content of oxygen in the waste gas emitted from it typically being 5-10%), there are three main treatment approaches: the HC-SCR process using hydrocarbons (HC) as the reducing agent, the NOₓ storage-reduction (NSR) process, and the urea-SCR method using NH₃ as the reducing agent. Selective reduction of NOₓ with hydrocarbons have been studied extensively because, for engines, HC chemical compounds are easily available, and substances of this type are usually contained in gas emitted from the engines. However, due to its activity and selectivity at the operation temperature, its negative effects are much higher than expected. For NSR process, NOₓ is stored in the catalyst during the normal lean operation stage of the engine, while regeneration of the
catalyst is carried out by short pulses of engine operation in the rich mode, and during these short periods, the NO\textsubscript{x} stored is released and reduced over noble metal surfaces. This process can bring about a very high NO\textsubscript{x} removal rate (>85%), but the remaining problem is that the NSR catalyst is extremely sensitive to SO\textsubscript{2}, and SO\textsubscript{2} in the exhaust gas will deactivate the catalyst, thus limiting its use to countries and regions where the content of sulfur in the fuel is very low. In view of this, many researchers have shifted their attention to vanadium oxide or zeolite catalyst for the selective reduction of NO\textsubscript{x} using ammonia.

[0005] Many catalysts for the selective catalytic reduction OfNO\textsubscript{x} in existing technologies are of the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} system. However, for catalysts of said type, upon heating (>600°C), because of the phase change of the TiO\textsubscript{2} support and sintering and volatilization of the active component V\textsubscript{2}O\textsubscript{5}, its thermal stability is poor.

[0006] Disclosed in U.S. Patent No. No. 5,552,128 are a series of ZrO\textsubscript{2} and WO\textsubscript{3} containing catalysts for the reduction of NO\textsubscript{x}. Yet these catalysts at low temperature only have a limited catalytic performance.

[0007] Therefore, there is a particular need for a new SCR catalyst that can be used to reduce the emission OfNO\textsubscript{x} from stationary sources and mobile sources, and that is highly active, with a wide temperature window, and having good thermal stability, with which human and animal health will not be affected during the reduction of NO\textsubscript{x} emission.

**SUMMARY OF THE INVENTION**

[0008] A first aspect of the present invention relates to a catalyst for the selective catalytic reduction of nitrogen oxides, characterized in that it comprises a first component and a second component that provides the first component with physical support and synergetic or auxiliary catalytic functions, wherein:

- the first component is selected from oxides of a transitional metal other than the metal contained in the second component, and mixtures and combinations thereof; the amount of the first component, based on the total weight of the first component and the second component, is from 0.1% to 30%;

- the second component is selected from cerium oxides, oxides of a lanthanide metal other than cerium, cerium-zirconium composite oxides, composite oxides of a lanthanide metal other than cerium and zirconium, cerium-titanium composite oxides, and composite oxides of a lanthanide metal other than cerium and titanium, and mixtures
and combinations thereof; the amount, in moles, of lanthanide atoms in the second component is at least 1% of the total amount, in moles, of the metal atoms in said second component, and the amount of the second component, based on oxides of the metals at the highest valency, is from 70% to 99.9% of the total weight of the first component and the second component.

[0009] In certain embodiments of the catalyst of the present invention, the content of the first component, based on the total weight of the first component and the second component, is from 5% to 20%. In certain other embodiments of the catalyst of the present invention, the content of the first component, based on the total weight of the first component and the second component, is from 6% to 15%.

[0010] In certain embodiments of the catalyst of the present invention, the first component is essentially distributed on the surface of the particles of the second component.

[0011] In certain embodiments of the catalyst of the present invention, the first component is selected from \( \text{Fe}_2\text{O}_3, \text{Cr}_2\text{O}_3, \text{MnO}_2, \text{V}_2\text{O}_5, \text{MoO}_3, \text{WO}_3 \), and mixtures and combinations thereof. In certain other embodiments of the catalyst of the present invention, the first component is selected from \( \text{MoO}_3, \text{WO}_3 \), and mixtures and combinations thereof. In still certain other embodiments of the catalyst of the present invention, the first component is \( \text{WO}_3 \).

[0012] In certain embodiments of the catalyst of the present invention, the second component is selected from cerium oxides, composite oxides of cerium and zirconium, and composite oxides of cerium and titanium, and mixtures and combinations thereof.

[0013] In certain embodiments of the catalyst of the present invention, the second component is a composite oxide of cerium and zirconium. Also, in certain embodiments of this type, the second component is a composite oxide of cerium and zirconium, and the molar ratio of cerium atoms to zirconium atoms in said second component is 0.01:1 to 10:1. In certain embodiments of this type, the second component is a composite oxide of cerium and zirconium, and the molar ratio of cerium atoms to zirconium atoms in the second component is 1:4 to 4:1. In certain other embodiments of this type, the second component is a composite oxide of cerium and zirconium, with the molar ratio of cerium atoms to zirconium atoms in the second component being 1:2 to 2:1. In still certain other embodiments of this type, the second component is a composite oxide of cerium and
zirconium, with the molar ratio of cerium atoms to zirconium atoms in the second component being 1.0:1.1 to 1.1:10.

[0014] In certain embodiments of the catalyst of the present invention, the second component is a nanocrystalline substance. In certain embodiments of the catalyst of the present invention, the mean particle size of the second component is 10-500 nanometers. In certain embodiments of the catalyst of the present invention, the mean particle size of the second component is 20-200 nanometers. In still certain other embodiments of the catalyst of the present invention, the mean particle size of the second component is 20-100 nanometers.

[0015] In certain embodiments of the catalyst of the present invention, the catalyst is in pellet form.

[0016] In certain embodiments of the catalyst of the present invention, said catalyst also contains an inert support, with the support being loaded with the first component and the second component as described above. In certain embodiments of this type, the first component is distributed on the surface of the particles of the second component, and the composite particles of said first component and second component are loaded on the surface of the inert support. In certain embodiments of this type, at least part of the first component and at least part of the second component are loaded on the surface of the inert support. In certain embodiments of this type: (1) part of the second component is distributed on the surface of the particles of the first component, with the composite particles of said first component and second component being loaded on the surface of the inert support; and (2) part of the first component and part of the second component are loaded on the surface of the inert support.

[0017] In certain embodiments of the catalyst of the present invention, said catalyst also contains a porous support; loaded on said support are the first component and the second component as described above. In certain embodiments of this type, said porous support may be an inert support as described above.

[0018] A second aspect of the present invention involves a process for making the various above-mentioned catalysts in pellet form, characterized in that it comprises the following steps:

(1) forming a precursor of the second component by co-precipitation of an aqueous solution, and calcining the precursor to obtain the second component;
loading a precursor of the first component on the second component obtained in Step (1).

In certain embodiments of the process for making the catalyst in pellet form in the present invention, Step (1) above comprises the following steps:

1. Preparing an aqueous dispersion containing a salt of cerium (such as a nitrate), a salt of zirconium (such as nitrate), and urea;
2. Preparing the precursor of the cerium-zirconium composite oxides by mixing and co-precipitating the aqueous dispersion obtained in Step (1); and
3. Calcining the precursor of the cerium-zirconium composite oxides obtained in Step (1B).

In certain embodiments of the process for making the catalyst in pellet form in the present invention, the cerium nitrate may be Ce(NO$_3$)$_3$ or (NH$_4$)$_2$Ce(NOs)$_6$; and the zirconium nitrate may be Zr(NO$_3$)$_4$.

In certain embodiments of the process for making the catalyst in pellet form in the present invention, Step (2) above comprises the following steps:

1A. Preparing an aqueous dispersion containing the precursor of the first component and the second component obtained in Step (1);
2B. Evaporating part of the solvent in said aqueous dispersion, to obtain a paste; and
3C. Drying and calcining the paste.

Certain embodiments for making the catalyst in pellet form in the present invention comprises the following steps: (i) preparing an aqueous dispersion comprising a salt of cerium, a salt of zirconium, a salt of tungsten and urea; (ii) heating the dispersion until it decomposes; and (iii) calcining the powder obtained in step (ii) to obtain a catalyst.

A third aspect of the present invention involves a first category process for making the various above-mentioned catalysts containing a porous support, characterized in that it includes:

(I) Preparing an aqueous dispersion of the second component;
(II) Impregnating the porous support with the aqueous dispersion of the second component prepared in Step (I);
(III) Drying and calcining the object treated in Step (II);
impregnating the object treated in Step (III) with an aqueous dispersion (including but not being limited to a solution form) containing the precursor of the first component; and

(V) drying and calcining the object treated in Step (FV).

In certain embodiments of the first category process for making the porous-support-containing catalyst of the present invention, Step (I) mentioned above includes:

(Ia) preparing the aqueous dispersion containing a salt of cerium (such as a nitrate), or a salt of zirconium (such as a nitrate);

(IB) adding ammonia to the aqueous dispersion obtained in Step (Ia) until a gel comprising cerium and zirconium is obtained; and

(IC) adding nitric acid into the gel obtained in Step (IB), to obtain a sol containing cerium and zirconium.

In certain embodiments of the first category process for making the porous-support-containing catalyst of the present invention, Step (I) mentioned above includes:

(Ia) preparing the powder of cerium-zirconium composite oxide;

(Ib) preparing the sol containing cerium and zirconium;

(Ic) mixing nitric acid, the cerium-zirconium composite oxide powder prepared in Step (Ia) and the sol containing cerium and zirconium prepared in Step (Ib), then grinding the mixture;

The slurry prepared from this is the aqueous dispersion of the second component.

In certain embodiments of the first category process for making the porous-support-containing catalyst of the present invention, Step (I) mentioned above includes:

(11) preparing an aqueous emulsion containing the surfactant (such as polyoxyethylene octylylphenyl ether), a co-surfactant (such as n-hexanol), and oil-phase solvent (such as cyclohexane), Ce(NO₃)₃ and Zr(NO₃)₄;

(12) preparing the aqueous emulsion containing polyoxyethylene octylylphenyl ether, a co-surfactant (such as n-hexanol), cyclohexylamine, and ammonia;

(13) mixing the aqueous emulsion prepared in Step (II) and the emulsion prepared in Step (12);

(14) separating the solid particles formed from the aqueous emulsion of Step (13);

(15) drying and calcining the solid particles obtained in Step (14);
(16) mixing the solid particles obtained in Step (15), the cerium-zirconium sol, and nitric acid, then grinding the mixture;

The slurry prepared from such is the aqueous dispersion of the second component.

A fourth aspect of the present invention involves a second category process for making the various above-mentioned catalysts comprising a porous support, characterized in that it includes:

   (1) preparing the aqueous suspension of the cerium-zirconium composite oxide powder;
   (2) adding the precursor of the first component to the suspension mentioned above;
   (3) heating the mixture prepared in Step (2) until most of the solvent is evaporated, obtaining a paste;
   (4) drying and calcining the paste prepared in Step (3), obtaining a powder;
   (5) grinding the mixture of the powder prepared in Step (4), cerium-zirconium sol, and nitric acid, obtaining a slurry;
   (6) impregnating the porous support with the slurry obtained in Step (5); and
   (7) drying and calcining the object treated in Step (6).

A fifth aspect of the present invention involves the use of the various catalysts mentioned above, characterized in that it is used for selective catalytic reduction of nitrogen oxides emitted from a stationery source or mobile source. In certain embodiments of the use of the catalyst of the present invention, said catalyst is used for the selective catalytic reduction of nitrogen oxides emitted from an internal combustion engine. In certain embodiments, ammonia or urea is used as a reducing agent.

Catalysts in some of the embodiments of the present invention have a fairly high hydrothermal stability and good thermal stability. Also, catalysts in some of the embodiments of the present invention are not significantly susceptible to adverse effects of substances such as SO₂, H₂O, CO₂, CO, and other hydrocarbon compounds, and they can maintain their catalytic activity in gas emission systems.

Catalysts in certain embodiments of the present invention essentially will not emit toxic metals in the process of use, so they are not hazards to human health.

Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in
the art from the description or recognized by practicing the invention as described in the
written description and claims hereof, as well as the appended drawings.

[0033] It is to be understood that the foregoing general description and the following
detailed description are merely exemplary of the invention, and are intended to provide
an overview or framework to understanding the nature and character of the invention as
it is claimed.

[0034] The accompanying drawings are included to provide a further understanding
of the invention, and are incorporated in and constitute a part of this specification.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0035] FIG. 1 is a diagram showing NO conversion rates as a function of
temperature of a series of catalysts according to certain embodiments of the present
invention, as well as a series of catalysts not according to the present invention, in pellet
form.

[0036] FIG. 2 is diagram showing NO and NH₃ conversion rates of the pellet-form
WO₃ZCe₀.₈Zr₀.₂O₂ (1/10) catalyst in certain embodiments of the present invention at
300°C, during a 200-hour testing period, and the concentration of N₂O in the reaction
effluent gas;

[0037] FIGS. 3A and 3B show NO conversion rates as a function of temperature of the
pellet-form WO₃/CeₓZr₁₋ₓO₂ catalyst in certain embodiments of the present invention
before and after aging.

[0038] FIG. 4 shows NO conversion rate as a function of temperature of the pellet-
form WO₃ZCe₀.₈Zr₀.₂O₂ catalyst prepared by means of an incipient wet impregnation
process in certain embodiments of the present invention.

[0039] FIG. 5A and 5B show NO conversion rate as a function of temperature of the
pellet-form WO₃ZCe₀.₅Zr₀.₅O₂ catalyst prepared by means of incipient wet impregnation
process in certain embodiments of the present invention in a reaction under programmed
temperature control, before and after aging.

[0040] FIG. 6 shows NOₓ conversion rate as a function of temperature of the pellet-
form WO₃ZCeₓTi₁₋ₓO₂ catalyst prepared by means of incipient wet impregnation process
in certain embodiments of the present invention.

[0041] FIG. 7 shows NO conversion rate as a function of temperature of the pellet-
form WO₃ZCe₀.₅Zr₀.₅O₂ catalyst prepared by means of impregnation process in certain
embodiments of the present invention after aging, when NO₂ is present in the influent gas.

[0042] FIG. 8 shows NO conversion rate as a function of temperature of the pellet-form W\(\theta_{3}/\text{CeO}_{5/2}\text{ZrO}_{5/2}\) catalyst prepared by means of combustion synthesis in certain embodiments of the present invention.

[0043] FIG. 9 shows NO conversion rate as a function of temperature of the pellet-form MoO₃ZCe₀.₅Zr₀.₅O₂ catalyst prepared by means of impregnation process in certain embodiments of the present invention.

[0044] FIG. 10 shows NO conversion rate as a function of temperature of the pellet-form CrO₃/Ce₀.₅Zr₀.₅O₂ catalyst prepared by means of impregnation process in certain embodiments of the present invention, before and after aging.

[0045] FIG. 11 shows NO conversion rate as a function of temperature of the pellet-form Fe₂O₃/Ce₀.₅Zr₀.₅O₂ catalyst prepared by means of impregnation process in certain embodiments of the present invention, before and after aging.

[0046] FIG. 12 shows NO conversion rate as a function of temperature of the pellet-form MnO₈/Ce₀.₅Zr₀.₅O₂ catalyst prepared by means of impregnation process in certain embodiments of the present invention, before and after aging.

[0047] FIG. 13 shows NO conversion rate as a function of temperature of the pellet-form V₂O₅/ZCe₀.₅Zr₀.₅O₂ catalyst prepared by means of impregnation process in certain embodiments of the present invention, before and after aging.

[0048] FIG. 14 show NO conversion rate as a function of temperature of the structured WO₃ZCe₀.₈Zr₀.₂O₂Zcordierite honeycomb ceramic catalysts having differing cell density in certain embodiments of the present invention.

[0049] FIG. 15 shows NO conversion rate as a function of temperature of a structured WO₃ZCe₀.₈Zr₀.₂O₂Zcordierite honeycomb ceramic catalyst in another embodiment of the present invention.

[0050] FIG. 16 shows NO conversion rate as a function of temperature of a structured WO₃ZCe₀.₅Zr₀.₅O₂Zcordierite honeycomb ceramic catalyst in another embodiment of the present invention.

[0051] FIG. 17 shows NO conversion rate as a function of temperature of a structured WO₃ZCe₀.₅Zr₀.₅O₂Zcordierite honeycomb ceramic catalyst in another embodiment of the present invention.
FIG. 18 shows and compares the performances of a series of catalysts of the present invention and those not of the present invention under certain testing conditions. FIG. 19 shows and compares the performances of a series of catalysts of the present invention and those not of the present invention under other certain testing conditions.

SPECIFIC EMBODIMENTS OF THE INVENTION

Unless otherwise indicated, all numbers such as those expressing weight percents of ingredients, dimensions, and values for certain physical properties used in the specification and claims are to be understood as being modified in all instances by the term "about." It should also be understood that the precise numerical values used in the specification and claims form additional embodiments of the invention. Efforts have been made to ensure the accuracy of the numerical values disclosed in the Examples. Any measured numerical value, however, can inherently contain certain errors resulting from the standard deviation found in its respective measuring technique. As used herein, in describing and claiming the present invention, the use of the indefinite article "a" or "an" means "at least one," and should not be limited to "only one" unless explicitly indicated to the contrary. Thus, for example, reference to "an alkali metal" includes embodiments having two or more such elements, unless the context clearly indicates otherwise.

Unless specified otherwise, the term "X, Y, Z, ... and combinations thereof" means a group consisting of the following elements: X, Y, Z, ..., and combinations of any 2, or more than 2 members of X, Y, Z, ..., at any proportion.

The term "nano-crystalline material" as used herein means a relevant material having a mean crystal size smaller than 500 nm.

The term "aqueous solution" or "aqueous dispersion" as used herein means a material system comprising water and with or without any other solvent. Therefore, an aqueous solution or an aqueous dispersion may also contain, in addition to water, other solvents such as an alcohol, and the like.

A "precursor of the first component" as used herein means a substance capable of dispersing in a material system to act as a source material for one or more oxides in the first component of the catalyst of the present invention. In certain embodiments, the precursor of the first component is a water-soluble salt of the relevant metal. Examples of such salt include, but are not limited to, ammonium metatungstate;
ammonium metamolybdate; ammonium vanadate; ammonium dichromate; iron nitrate; manganese nitrate, and the like.

A "precursor of the second component" as used herein means a substance capable of dispersing in a material system to act as a source material for one or more oxides in the second component of the catalyst of the present invention. In certain embodiments, the precursor of the second component is a water-soluble salt of the relevant metal. Examples of such salt include, but are not limited to: cerium nitrate; zirconium nitrate; ammonium cerium nitrate, and the like.

The term "Ce-Zr sol" as used herein means a material system comprising Ce and Zr-containing colloidal particles having a mean particle size of 1-100 nm dispersed therein. The pH of such material is typically acidic. In certain embodiments, the pH thereof is from 1 to 5. In certain other embodiments, the pH thereof is from 1 to 1.5.

The term "composite oxides" as used herein means a mixture of oxides of two or more metal elements.

"Pellet catalyst" described in the present invention in general refers to the catalyst packed in an irregular manner in the reactor when being used. The geometric configuration of a pellet catalyst may be, but is not restricted to, spherical, cylindrical, flake-like, or powdery.

"Structured catalyst" as used herein in general refers to a catalyst arranged in a regular manner in the reactor when being used. The geometric configuration of a structured catalyst may be, but is not restricted to, a honeycomb, a foam, a corrugated metal plate, and the like. The catalyst can be prepared in such a way that the active component of the catalyst is loaded in the form of a wash coat onto the surface or the channels of the support; it can also be prepared in such a manner as to extrude the active component of the catalyst as a structured unit.

In all of the appended drawings, \( C_{NO} \) indicates NO conversion rate; \( T \) indicates the temperature.

Without intending to be bound by a particular theory, it is believed that the first component of the catalyst of the present invention provides the active site. For the SCR reaction on the catalyst provided by the present invention, ammonia is adsorbed onto the active site of the first component (which may be a Bronsted acid or Lewis acid). Upon electron transfer to the active site, hydrogen integrated with nitrogen molecules by means of a covalent bond in ammonia is activated. As the reaction proceeds, ammonia
molecules are activated and dehydrogenated, reacting with NO\textsubscript{x} in the gas phase, forming non-toxic nitrogen and water via the Rideal mechanism. After the reaction, the metal center in the active site is reduced, and needs to undergo oxidation before entering the next cycle.

[0066] It is known that due to the oxygen-storage capacity, oxygen-release capacity, and oxygen transfer capability of cerium dioxide and cerium-zirconium composite oxides, they have active synergistic effects in the three-way catalytic reaction. Based on the mechanism mentioned above, the oxidation and reduction activity of these materials can be used for a SCR catalyst; after the SCR reaction, the active site needs to undergo oxidation at a relatively low temperature.

[0067] The first component of the catalyst based on the present invention has two characteristics: acidity and activity associated with oxidation and reduction. Being acidic allows for the adsorption of ammonia at operating temperatures. The oxidation and reduction activity relates to activation of the ammonia molecule adsorbed, while activation of ammonia requires a transfer of hydrogen atoms. To meet the requirements mentioned above, in certain embodiments, the first component of the catalyst may be selected from: Fe\textsubscript{2}O\textsubscript{3}, MnO\textsubscript{2}, CrO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, MoO\textsubscript{3}, and WO\textsubscript{3}. The metal elements in the first component are mainly present in the catalyst of the present invention in the form of oxides. The valency of said metal element is not limited to one value only. For example, tungsten may be present in the +6 valency (such as WO\textsubscript{4}\textsuperscript{2-}, WO\textsubscript{3}, etc.), +4 valency (such as WO\textsubscript{3}\textsuperscript{2-}, WO\textsubscript{2} etc.), or another valency. Also, vanadium may be present in the +5, +4, +3, or other valency. Besides, part of the first component may also be combined through chemical or physical means, with other components of the catalyst, such as the second component, a support, a small amount of water, etc. For the sake of convenience, the total amount of the first component or the subtotal amount of the various components refer to the total amount of all of the relevant metals in various states, but will be calculated and indicated only in the forms selected above (Fe\textsubscript{2}O\textsubscript{3}, MnO\textsubscript{2}, CrO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, MoO\textsubscript{3}, and WO\textsubscript{3}). The first component contains OH surface groups, which can be combined with molecules of ammonia compounds and derivatives thereof (nitrogen-containing substances with a low nitrogen valency, such as NH\textsubscript{3}, NH\textsubscript{2}NH\textsubscript{2}, urea, etc.) in the waste gas to be treated. Upon oxidation and reduction, ammonia is transformed into the active state in the SCR reaction.
[0068] As discussed above, the catalyst of the present invention may contain Fe₂O₃, MnO₂, CrO₃, and/or V₂O₅ as part or all of the first component. In certain advantageous embodiments of the present invention, the first component mainly contains WO₃, MoO₃, or their combinations in various proportions. In certain other advantageous embodiments of the present invention, the first component mainly contains WO₃.

[0069] In the catalyst of the present invention, the content of the first component based on the total weight of the first component and the second component is 0.1%-20%, or is 1%-20% in certain embodiments, 2%-20% in certain other embodiments, 5%-18% in certain other embodiments, 8%-18% in certain other embodiments, 10%-18% in certain other embodiments, 10%-17% in certain other embodiments, 5%-20% in certain other embodiments, or 6%-15% in certain other embodiments. Data indicate that when the content of the first component is 10% to 18%, said catalyst has a good nitrogen monoxide conversion rate.

[0070] In view of the fact that the first component requires direct contact with the gas to be treated, the first component must at least be partially distributed on the surface of the catalyst of the present invention. However, it is not ruled out that part of the first component can be distributed inside the particles of the second component, inside the support material other than the first component and the second component, or on the surface of said support (if said support is present). In certain embodiments of the present invention, the first component is essentially distributed (for example, at least 50%, including 60%, 70%, 80%, and even 90%) on the surface of the particles of the second component. In certain other embodiments of the present invention, the first component is partially distributed on the surface of the particles of the second component, and partially distributed on the surface of the support.

[0071] The second component not only provides a physical support for the first component, but also plays a synergistic or auxiliary catalytic action with respect to the first component. Without intending to be bound by a particular theory, it is believed that the second component accomplishes adsorption and activation of ammonia synergistically with the first component at low temperature.

[0072] The second component of the catalyst of the present invention is selected from: cerium oxides, oxides of a lanthanide metal other than cerium, cerium-zirconium composite oxides, composite oxides of a lanthanide metal other than cerium and zirconium, cerium-titanium composite oxides, composite oxides of a lanthanide metal
other than cerium and titanium, and mixtures or combinations thereof. In certain embodiments of the present invention, the second component is selected from cerium oxides, cerium-zirconium composite oxides, cerium - titanium composite oxides, and mixtures or combinations thereof. In certain other embodiments of the present invention, the second component is a cerium-zirconium composite oxide.

[0073] In the catalyst of the present invention, based on the total weight of the first component and the second component, and calculated in terms of the oxide in the highest valency state, the content of the second component is 70%-99.9%, or is 80%-99% in certain embodiments, 80%-98% in certain other embodiments, 82%-95% in certain other embodiments, 82%-92% in certain other embodiments, 82%-90% in certain other embodiments, and 83%-92% in certain other embodiments.

[0074] In the second component, cerium or some other lanthanide metal provides the required storage function and oxygen-supplying function. If there is a metal oxide other than that of a lanthanide, such as zirconium or titanium oxides, their function is mainly to enhance the stability of the catalyst.

[0075] Because the reaction of the catalyst of the present invention with nitrogen oxide takes place on the gas phase-solid phase interface, the specific surface area of the catalyst has a very important effect on its catalytic activity. Within a certain range, the more the first component is distributed at the gas phase-solid phase interface, the higher the activity of the catalyst. Therefore, the larger the specific surface area of the support used for the first component, the higher the activity of the catalyst up to a certain level. The stability of the catalytic activity is directly related to the stability of the specific surface area of the support used for the first component. If the catalyst in the process used will be subjected to heat, the thermal stability of the support used for the first component has direct effects on the thermal stability of the catalyst. As mentioned above, the second component of the catalyst provides a physical support for the first component. Therefore, for a high catalytic performance, the second component should have a higher specific surface area; also, to maintain the stability of the general performance of the catalyst, the specific surface area of the second component should maintain a certain level of stability.

[0076] In certain embodiments of the catalyst of the present invention, the second component comprises a nanocrystalline material. In these embodiments, the mean particle size of the second component is 1-500 nm; in certain other embodiments, the
mean crystal particle size of the particles of the second component is 1-200 nm, and in still certain other embodiments, the mean crystal particle size of the nanocrystalline material is 1-100 nm. In certain embodiments, the specific surface area of the particle of the second component is at least 70 m²·g⁻¹; in certain other embodiments the specific surface area of the particle of the second component is at least 100 m²·g⁻¹.

[0077] In terms of the thermal stability of the catalyst at an elevated temperature, the second component not only needs to maintain a high specific surface area, but also needs to maintain a certain level of oxidation and reduction capacity upon exposure to an elevated temperature. Without intending to be bound by a particular theory, it is believed that oxides of lanthanides such as cerium oxide are capable of undergoing a rapid cycle of oxidation and reduction (Ce⁴⁺ ↔ Ce³⁺), with its oxygen storage and release function being highly associated with its specific surface area—the greater the specific surface area, the better the oxygen storage and release performance will be. Besides, after cerium oxide is mixed with zirconium oxide, more defects and an oxygen ion vacancy will be formed; also, the activation energy associated with the diffusion of the oxygen ions will be reduced, thus enhancing the oxidation and reduction performance of the catalyst at low temperature.

[0078] If the second component contains only fine particles of pure cerium oxide, in certain embodiments it still has a high initial activity for nitrogen oxide conversion. However, in certain embodiments, pure cerium oxide particles will be sintered upon heating, the crystal particles will grow rapidly, and the specific surface area will decrease significantly, resulting in a decrease in the oxidation and reduction performance. Therefore, catalysts whose second component contains only cerium oxide are not the most favorable for use under elevated temperatures (such as some exhaust-gas purification devices for a diesel engine, whose operation temperature is as high as 700-800°C). There is consistently a need to add a heat stabilizer to these catalysts to meet the stability requirement.

[0079] Experiments indicate that zirconium oxide can lead to the stabilization of cerium oxide thoroughly mixed with it at an elevated temperature. Heat-sintering resistance performance of cerium-zirconium composite oxides is manifestly better than that of cerium oxides, which is why the thermal stability of the catalyst can be significantly enhanced. In certain embodiments of the catalyst of the present invention, for a balance between thermal stability and high activity, the second component is a
composite oxide of cerium and zirconium, and the mole ratio of cerium atoms to zirconium atoms in the second component is 0.01:1 to 10:1. In certain embodiments of this type, the second component is a composite oxide of cerium and zirconium, and the mole ratio of cerium atoms to zirconium atoms in the second component is 1:4 to 4:1. In certain other embodiments of this type, the second component is a composite oxide of cerium and zirconium, and the mole ratio of cerium atoms to zirconium atoms in the second component is 1:2 to 2:1. In still certain other embodiments of this type, the second component is a composite oxide of cerium and zirconium, and the mole ratio of cerium atoms to zirconium atoms in the second component is 1.0:1.1 to 1.1:10. In certain embodiments of this type, the cerium-zirconium composite oxide consists of a nanocrystalline material as mentioned above. The cerium-zirconium composite oxide with the nano structure provides the required surface area and thermal stability; it also provides the required oxidation and reduction capacity.

[0080] In certain embodiments of the catalyst of the present invention, for the balance between thermal stability and high activity, the second component is essentially a single-phase crystalline material of composite oxides. By "single-phase" is meant that the characteristic peaks of the individual oxides cannot be all observed on an XRD spectrum. Without intending to be bound by a particular theory, it is believed that in single-phase composite oxides, when one oxide forms crystals, the other oxide enters the crystal lattice to form a homogenous mixture. In certain embodiments, in said composite oxide, phase separation at the scale of 100 nm cannot be observed. Also, in certain embodiments of this type, phase separation at the scale of 10 nm cannot be observed in said composite oxide. Single-phase composite oxides, particularly single-phase cerium-zirconium composite oxides, have a fairly good thermal stability that is better than that of multi-phase mixtures of oxides.

[0081] In certain embodiments of the catalyst of the present invention, after the second component is calcined at 800°C for 1 (one) hour, the enlargement of the crystal particles does not exceed 20%; it does not exceed 10% in certain other embodiments, it does not exceed 5% in certain other embodiments, it does not exceed 3% in certain other embodiments, it does not exceed 2% in certain other embodiments, and it does not exceed 1% in certain other embodiments.

[0082] In certain embodiments of the present invention, said catalyst is present in the form of pellets. In certain embodiments, said pellets essentially consist of a first
component and a second component. In certain embodiments, said pellets also contain, in addition to the first component and the second component, an inert support (inorganic glass, inorganic ceramic, metals, refractory materials, etc.), and the first component and the second component are respectively loaded on it. The catalyst in pellet form can be used in a packed-bed reactor.

[0083] In certain embodiments of the present invention, the catalyst further comprises a porous support, and the first component and the second component are loaded respectively on the surface of the porous support. In certain embodiments, said porous support is a structured honeycomb support. Said support may be composed of the following materials: inorganic glass, inorganic ceramic, metals, refractory materials, etc. (such as honeycomb ceramics, foam ceramic, or metal honeycomb, etc.). A coated honeycomb-shaped catalyst may be employed to treat waste gas emitted from a stationery source or a mobile source, such as the waste gas emitted from a diesel engine or direct-injection gas engine. In certain embodiments of this type, the first component is loaded on the surface of the particles of the second component, while the composite particles of said first component and second component are loaded on the surface of the porous support. In certain other embodiments of this type, part of the first component is loaded on the surface of the particles of the second component, composite particles of said first component and second component are loaded on the surface of the porous support, while another part of the first component is directly loaded on the surface of the porous support.

[0084] Also provided in the present invention is a process for making the catalyst for the selective catalytic reduction of nitrogen oxides, which includes preparation of the first component from the precursor of said first component, preparation of the second component using chemical synthesis techniques such as the process of precipitation, the process of homogeneous precipitation, and the microemulsion process, etc., then loading the first component onto the second component by impregnation, precipitation, and other techniques.

[0085] Also provided in the present invention is a process for making the catalyst for the selective catalytic reduction of nitrogen oxides, wherein through the process of solution combustion synthesis, a catalyst containing the first component and the second component is prepared in one step. Certain embodiments of processes of this type include the following steps: (i) preparation of an aqueous dispersion of a cerium-
containing salt (such as cerium nitrate), zirconium nitrate, tungsten-containing salt, and urea; and (ii) heating the aqueous dispersion prepared in Step (i) until it is decomposed. [0086] In certain embodiments of the various processes of preparation of the various catalysts of the present invention, the first component may be loaded onto the surface of the second component by means of the process of equal-volume impregnation or excess impregnation. As mentioned above, in certain embodiments, for the optimal result, the particles of the second components are nanocrystalline material. A nanocrystalline material can be prepared through several types of chemical synthesis, including the process of co-precipitation, the process of homogenous precipitation, the process of microemulsion precipitation, and the process of solution combustion synthesis, as long as the material produced is an oxygen storage material capable of high oxygen conductivity at low temperature. The first component may be derived from various precursors, such as oxides or salts. The first component may be coated onto the auxiliary support by means of impregnation, precipitation, or other techniques. [0087] In certain embodiments of the present invention, the catalyst in pellet form can be prepared by the following processes:

(1) Through the process of co-precipitation of the aqueous solution, the precursor of the second component is prepared; also, through calcining said precursor, the second component is prepared;

(2) The precursor of the first component is loaded onto the second component prepared in Step (1) mentioned above.

[0088] In certain embodiments, Step (1) mentioned above includes the following steps:

(IA) Preparing an aqueous dispersion containing a salt of cerium (such as a nitrate), a salt of zirconium (such as a nitrate), and urea;

(IB) Preparing the precursor of the cerium-zirconium composite oxides by means of mixing and co-precipitating the aqueous dispersion obtained in Step (IA);

(1C) Calcining the precursor of the cerium-zirconium composite oxides obtained in Step (IB).

[0089] In certain embodiments of this type, the cerium nitrate may be Ce(NO$_3$)$_3$ or (NH$_4$)$_2$Ce(NO$_3$)$_6$; the zirconium nitrate may be Zr(NO$_3$)$_4$.

[0090] In certain embodiments of this type, Step (2) above comprises the following steps:
(2A) Preparing an aqueous dispersion containing the precursor of the first component and the second component obtained in Step (1);

(2B) Evaporating part of the solvent in said aqueous dispersion, obtaining a paste;

(2C) Drying and calcining said paste.

[0091] For example, one of the specific processes to prepare the catalyst in pellet form may be: (A) Preparing a stock solution from salts selected from those of titanium, cerium, or zirconium elements or their combination (such as a solution prepared from the mixture of a certain amount of Ce(NO₃)₃ solution, Zr(NO₃)₄ solution, and urea with its cation concentration of 0.1-0.3 mole/L), stirring and heating to its boiling point, until co-precipitation can be observed; the precipitate obtained is then aged at the boiling point, then stirred at room temperature; said precipitate is filtered and washed, then dried at 50-80°C for 10-20 hours. Next, the dried precipitate is calcined at 400-600°C for 1-3 hours, and the support material is obtained; (B) Loading the salt made from V, Cr, Nb, Ta, Cr, Mo, W, Mn, and Fe elements to serve as the active component onto the support material obtained from Step (A) mentioned above; (C) The powder obtained from Step (B) is pressed and ground; those powder particles of 20-30 mesh are selected through screening, and can serve as the catalyst that can be used directly. The process using the support described may be such that: The support material obtained in Step (A) mentioned above is prepared into a powder, which is stirred and suspended in deionized water, then the salt made from V, Mo, W, Mn, and Fe elements serves as the active component, or a solution of the salt is added to the mixed suspension mentioned above; the mixture obtained is heated to 80-90°C, being heated and stirred continuously, until most of the moisture evaporates, obtaining a paste. The paste is dried at 100-150 0°C for 5-20 hours, then the dried sample is calcined at 400–600 0°C for 1–3 hours. The process using the support described may also be such that: The catalyst support particles of 20-30 mesh obtained in Step (A) are impregnated using the salt made from V, Cr, Mo, W, Mn, and Fe elements to serve as the active component, or using a solution of the salt, the particles are dried at room temperature for 3–9 hours, then at 100-150 0°C for 2-8 hours, then calcined at 400-600 0°C for 1-3 hours.

[0092] In certain embodiments of the present invention, the various catalysts mentioned above that contain the porous support may be prepared through a first category process listed below:
(I) Preparation of the aqueous dispersion of the second component;
(II) Impregnating of the porous support with the aqueous dispersion of the second component prepared in Step (I);
(III) Drying and calcining the object treated in Step (II);
(FV) Impregnating the object treated in Step (III) with the aqueous dispersion containing the precursor of the first component;
(V) Drying and calcining the object treated in Step (FV).

[0093] In certain embodiments of this type, Step (I) mentioned above includes:
(IA) Preparing the aqueous dispersion containing a salt of cerium (such as a nitrate) or a salt of zirconium (such as a nitrate);
(IB) Adding ammonia to the aqueous dispersion obtained in Step (IA) until a gel comprising cerium and zirconium is obtained;
(IC) Adding nitric acid to the gel obtained in Step (IB), to obtain a sol containing cerium and zirconium.

[0094] In certain embodiments of the first type, Step (I) mentioned above includes:
(Ia) Preparing the powder of cerium-zirconium composite oxide;
(lb) Preparing the sol containing cerium and zirconium;
(ic) Mixing nitric acid, the cerium-zirconium composite oxide powder prepared in Step (Ia), and the sol containing cerium and zirconium prepared in Step (lb), then grinding the mixture;

[0095] The slurry prepared from such is the aqueous dispersion of the second component.

[0096] In certain embodiments of the first type, Step (I) mentioned above includes:
(11) Preparing an aqueous emulsion containing polyoxyethylene octylphenyl ether, a co-surfactant (such as n-hexanol), an oil-phase solvent (such as cyclohexane), Ce(NO$_3$)$_3$ and Zr(NO$_3$)$_4$;
(12) Preparing an aqueous emulsion containing polyoxyethylene octylphenyl ether, a co-surfactant (such as n-hexanol), cyclohexylamine, and ammonia;
(13) Mixing the aqueous emulsion prepared in Step (II) and the emulsion prepared in Step (12);
(14) Separating the solid particles formed from the aqueous emulsion of Step (13);
(15) Drying and calcining the solid particles obtained in Step (14);
Mixing the solid particles obtained in Step (15), the cerium-zirconium sol, and nitric acid, then grinding the mixture;

[0097] The slurry prepared from such is the aqueous dispersion of the second component.

[0098] The porous support may be a honeycomb-type ceramic, including but not limited to a cordierite honeycomb ceramic. One of the specific examples of the process of the first type used to prepare the catalyst containing a porous support may include: (I) Preparing the Ce-Zr dispersion; (II) Impregnating the honeycomb ceramic using the Ce-Zr dispersion obtained in Step (I), then removing the residual dispersion in the honeycomb passageway using hot air; after the removal is complete, the sample is dried, then calcined at 400-600°C for 1-3 hours, and this step is repeated three to nine times; (III) Impregnating the material obtained in Step (II) using the salt solution of the active component selected from V, Cr, Mo, W, Mn, and Fe elements, then removing the residual solution in the honeycomb passageway using hot air; after the removal is complete, the sample is dried, then calcined at 400-600 °C for 1-3 hours. Also, the process used to prepare the Ce-Zr dispersion described in Step (I) may include: Mixing the Ce(NO$_3$)$_3$ solution and Zr(NO$_3$)$_4$ solution, then adding aqueous ammonia (ammonium hydroxide) droplets into the Ce-Zr solution, with stirring, obtaining a Ce-Zr gel. Next, with stirring, HNO$_3$ is added to the gel, and the mixture is stirred for 6-10 hours, obtaining a Ce-Zr sol. The process used to prepare the Ce-Zr dispersion described in Step (I) may also include: The cerium-zirconium composite oxide (such as Ce$_{0.5}$Zr$_{0.2}$O$_2$ powder), Ce-Zr sol, and nitric acid (pH = 1.2) are mixed, then this mixture is ground using ball milling for 12-24 hours, obtaining a Ce-Zr slurry. The process used to prepare the Ce-Zr dispersion described in Step (I) may also include: (1) Polyoxyethylene octylphenyl ether and n-hexanol are added to cyclohexane, until the solution mixture becomes clear, then Ce(NO$_3$)$_3$ and Zr(NO$_3$)$_4$ solutions are added to the solution mixture and stirred until the solution becomes clear again; (2) Polyoxyethylene octylphenyl ether and n-hexanol are added at room temperature into cyclohexane, with stirring, to n-hexane, until the solution mixture becomes clear, then an ammonium hydroxide solution is added to the solution mixture and stirred, until the solution becomes clear again; (3) The microemulsions obtained from Step (1) and Step (2) are mixed, and the mixture is reacted with stirring for 10-60 minutes, then the microparticles are separated and vacuum-dried at 80-90 °C for 5-20 hours; the dried sample is calcined at 400-600 °C for
1-3 hours; (4) The powder obtained from Step (3), Ce-Zr sol, nitric acid (pH=1.2), and water are ground using ball milling for 10-60 minutes, obtaining the desired slurry comprising cerium-zirconium composite oxide.

[0099] The fourth aspect of the present invention relates to a second category of process for making the various above-mentioned catalysts that contain the porous support, characterized in that it includes:

1. Preparing the aqueous suspension of the cerium-zirconium composite oxide powder;

2. Adding the precursor of the first component to the suspension mentioned above;

3. Heating the mixture prepared in Step (2) until most of the solvent is evaporated, obtaining a paste;

4. Drying and calcining the paste prepared in Step (3), obtaining a powder;

5. Grinding the mixture of the powder prepared in Step (4), cerium-zirconium sol, and nitric acid, obtaining a slurry;

6. Impregnating the porous support with the slurry obtained in Step (5); and

7. Drying and calcining the object treated in Step (6).

[0010] Specific examples of the process of the first type to prepare the catalyst containing a porous support may be: (A) With stirring, the cerium-zirconium composite oxide (such as Ce$_{0.5}$Zr$_{0.5}$O$_2$) powder is mixed and suspended in water, then ammonium metatungstate is added to the mixed suspension; the mixture obtained is heated to 70–100°C, heated continuously and with stirring, until most of the moisture evaporates, obtaining a paste. The paste is dried at 120°C for 6–12 hours, then the dried sample is calcined at 400-600°C for 1-3 hours. (B) The powder obtained from Step (1), Ce-Zr sol, and nitric acid (pH = 1.2) are ground using a ball miller for 12—24 hours, and the slurry of WCVCerium-zirconium composite oxide (such as WO$_2$ZCe$_{0.5}$Zr$_{0.5}$O$_2$) is obtained; (C) The honeycomb ceramic is impregnated using the slurry obtained in Step (2), then the residual slurry in the honeycomb passageway is removed using hot air; after the removal is complete, the sample is dried, then calcined at 400-600°C for 1–4 hours; this step is repeated three to nine times.

[0011] The following non-limiting examples further illustrate the present invention as claimed.
EXAMPLES

[00102] At least part of the experimental results of the examples of the present invention are shown in the appended drawings. The connotations of the marks and symbols in all of the attached drawings are as follows: CNO (%) indicates the conversion rate (%) of NO; CN₂O ppm indicates the concentration (ppm) of N₂O at the gas outlet; T (°C) indicates the temperature; t (Hr) indicates the time (hours); and CNOₓ (%) indicates the conversion rate (%) OfNOₓ.

[00103] Example 1

[00104] Preparation of WO₃/CeₓZr₁₋ₓO₂ pellet catalyst using the process of impregnation, and characterization thereof

[00105] The composite oxides of the second component CeₓZr₁₋ₓO₂ (x = 0.2; 0.66; 0.8) were prepared using the following process.

[00106] Aqueous solutions of Ce(NO₃)₃ and Zr(NO₃)₄ at a concentration of 2 mol/L were prepared. 2000 ml of a solution with the total cation concentration of 0.1 mol/L was prepared from a certain amount of the Ce(NO₃)₃ solution and Zr(NO₃)₄ solution prepared as mentioned above, along with urea and deionized water, with the mole ratio of Ce³⁺:Zr⁴⁺:urea = x:(1 - x):15 (x = 0.2; 0.66; 0.8). With stirring, said solution was heated to its boiling point, until a precipitate formed. The mixture obtained was then aged at the boiling point for 2 hours, then stirred at room temperature for 2 hours. The precipitate was filtered, then washed with stirring using deionized water for 15 minutes. This step was repeated three times. The filter cake was then eluted with isopropanol using a Buchner funnel. After excess isopropanol was removed through filtering, the precipitate obtained was placed in a vacuum oven dryer, where it was dried at 60°C for approximately 15 hours. This dried precipitate was then calcined at 500°C in a furnace for 2 hours, so that it decomposed to form a CeₓZr₁₋ₓO₂ oxide.

[00107] Pure ZrO₂ was prepared using the same process, with pure CeO₂ being prepared by the decomposition of Ce(NO₃)₃·H₂O at 500°C.

[00108] The WO₃CexZryO₂ (x = 0; 0.2; 0.66; 0.8; 1) catalysts were synthesized using the process of impregnation. Step 1, dissolution of 3.45 g of (NH₄)₃H₅[W₂(O₄)₆]·H₂O using 70 ml OfNH₃·H₂O (12.5%). Step 2, for preparation of the catalyst, first, 30 g of CeₓZr₁₋ₓO₂ powder was mixed and suspended in 100 ml of deionized water with stirring. The solution prepared in Step 1 was then added to the suspension mentioned above, and the mixture obtained was heated in an oil bath to 85°C.
It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred into an oven dryer, where it was dried at 120°C overnight. The dried sample was calcined at 500°C for 2 hours, and a W(VCeₓZrₓ)O₂ catalyst, with WO₃:CeₓZr₁ₓX= 1:10 (weight ratio), was obtained. The powder was pressed, then ground, and those particles of 20–30 mesh were selected by screening.

An assessment of the SCR activity of the WO₃/CeₓZr₁ₓO₂ catalyst was made using a quartz fixed-bed reactor. In the tests, 1 ml of the catalyst of 20–30 mesh was used, and the composition of feedstock gas was 500 ppm NO, 500 ppm NH₃, 5% O₂ and balance N₂ (hereinafter "Feedstock Gas A"). The gas flow rate was set at 1.5 L/minute (STP) and the space velocity was 90000 IT⁻¹. The SCR activity as a function of temperature of the catalyst was determined. The concentration of the gas was measured using a Fourier Transform Infrared (FTIR) spectrometer with a 10-m optical path gas cell (Nicolet Nexus 470 model, DTGS detector). An FTIR spectrometer can rapidly determine the concentration of several gases on-line, including NO, NO₂, N₂O, and NH₃. Concentrations of various gases could be quantified using QuantPad software. Said software is based on CLS processing (classical least-squares fitting), and can correct the spectral absorption in the non-linear zone. For test results, see FIG. 1. In FIG. 1, Curve 1-1 shows NO conversion rate as a function of temperature on the WO₃/CeₓZr₁ₓO₂ (x = 0.2) catalyst. Curve 1-2 shows NO conversion rate as a function of temperature on the WO₃/CeₓZr₁ₓO₂ (x = 0.66) catalyst. Curve 1-3 shows NO conversion rate as a function of temperature on the WO₃/CeₓZr₁ₓO₂ (x = 0.8) catalyst. Curve 1-4 shows NO conversion rate as a function of temperature on the WO₃/CeO₂ catalyst, and Curve 1-5 shows NO conversion rate as a function of temperature on the WO₃/ZrO₂ catalyst.

The curves in FIG. 1 clearly indicate that some catalysts provided in accordance with certain embodiments of the present invention had very good SCR activity; also, with some catalysts such as WO₃/CeₓZr₁ₓO₂ (x = 0.8, 0.66), at a low temperature of 200°C, NO conversion rate reached higher than 75%, and at 250°C, NO approached complete conversion. The WO₃/CeₓZr₁ₓO₂ (x = 0.8) catalyst also had a very wide temperature window; also, from 250 to 400°C, NO conversion rate was consistently maintained at over 97%. At a temperature higher than 400°C, because the rate of the oxidation reaction between NH₃ and O₂ increased, more NH₃ was oxidized by O₂ instead of participating in the reduction reaction of NO, so NO conversion rate began to decline.
However, with some catalysts such as $\text{WO}_3Z\text{Ce}_x\text{Zr}_Lx\text{O}_2$ (\(x = 0.2, 0.8, 1\)), at 450°C NO conversion rate could still be maintained at over 80%. The functional temperature range could be adjusted and controlled by altering the Ce/Zr ratio in the second component. For comparison, the drawing also shows NO conversion rate on a $\text{WO}_3\text{ZrO}_2$ sample without containing CeO\(_2\), wherein at a high temperature (> 400°C), said sample shows a certain catalytic activity, as its NO conversion rate at 450°C can reach 78%; however, at a low temperature (below 300°C), said sample almost has no catalytic activity, and its NO conversion rate is extremely low (approximately 10%).

[00111] **Example 2**

[00112] **Characterization of the long-term stability of $\text{WO}_3\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ HZIO) pellet catalyst at 300°C**

[00113] A $\text{WO}_3\text{ZCe}_{0.8}\text{Zr}_{0.2}\text{O}_2$ catalyst with a $\text{WO}_3: \text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2 = 1:10$ (weight ratio) was prepared in the same way as in Example 1 mentioned above. The stability of the catalyst was examined via the SCR reaction at 300°C for 200 hour. The test conditions were the same as in Example 1 mentioned above. See FIG. 2 for test results. In FIG. 2, Curve 2-1 shows NO conversion rate for a test period of 200 hours, Curve 2-2 shows the NH\(_3\) conversion rate for a test period of 200 hours, and Curve 2-3 shows the concentration of the N\(_2\)O in the reaction effluent gas for a test period of 200 hours.

[00114] The curves in FIG. 2 clearly indicate that in the 200-hour stability test, the activity of the catalyst tested remained stable; NO conversion rate was kept at 96%, the NH\(_3\) conversion rate was kept constant at 100%, there was only a small amount of N\(_2\)O produced in the reaction process, and the N\(_2\)O concentration at the outlet was kept at 9—10 ppm. Most of the NO was converted to N\(_2\), which is harmless.

[00115] **Example 3**

[00116] **Preparation of $\text{WO}_3\text{Ce}_{x}\text{Zr}_{1-x}\text{O}_2$ pellet catalyst using the process of impregnation, and characterization of its performance before and after aging**

[00117] The process used to prepare the composite oxides of the second component $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ (\(x = 0.2; 0.5; 0.8\)) was the same as in Example 1 mentioned above, but (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) was used in place of Ce(NO\(_3\))\(_3\) as the precursor of CeO\(_2\). 2000 ml of a solution with the total cation concentration of 0.2 mol/L was prepared from a certain amount of (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) solution, Zr(NO\(_4\))\(_4\) solution and urea, with the mole ratio of $\text{Ce}^{4+}:\text{Zr}^{4+}:\text{urea} = (1-x):x:15$ (\(x = 0.2; 0.5; 0.8\)). With stirring, said solution was heated
to its boiling point, until a precipitate was observed. The mixture obtained was then aged at the boiling point for 2 hours, then stirred at room temperature for 2 hours. The precipitate was filtered, then washed with stirring using 1,500 ml of deionized water, for 15 minutes. This step was repeated three times. The filter cake was then eluted with 300 ml of isopropanol using a Buchner funnel. After excess isopropanol was removed through filtering, the precipitate obtained was placed in a vacuum oven dryer, where it was dried at 60°C for approximately 15 hours. The dried precipitate was then calcined at 500°C in a furnace for 2 hours, so that it decomposed to form a CeₓZr₁₋ₓO₂ oxide.

[0018] A W(VCeₓZr₁₋ₓO₂ (x = 0.2; 0.5; 0.8) catalyst was synthesized using the process of impregnation. First of all, with stirring, 15 g of CeₓZr₁₋ₓO₂ (x = 0.2; 0.5; 0.8) powder was mixed and suspended in 50 ml of deionized water. Next, 1.7647 g of ammonium metatungstate (NH₄WO₄) was added to the suspension mentioned above, then the mixture obtained was heated in an oil bath to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer where it was dried at 120°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a WO₃CeₓZr₁₋ₓO₂ (x = 0.2; 0.5; 0.8) catalyst, with WO₃:CeₓZr₁₋ₓO₂ (x = 0.2; 0.5; 0.8) = 1:10 (weight ratio), was obtained. The powder was pressed, then ground, with powder particles of 20-30 mesh being selected through screening.

[0019] An assessment of the SCR activity of the WO₃CeₓZr₁₋ₓO₂ (x = 0.2; 0.5; 0.8) catalyst was made using a quartz fixed-bed reactor. In the tests, 1 ml of the catalyst of 20—30 mesh was used; the composition of the feedstock gas was a simulation of the composition of the exhaust gas of a diesel engine, which was: 550 ppm NO; 550 ppm NH₃, 6% O₂, 10% CO₂, 10% H₂O and balance N₂ (hereinafter "Feedstock Gas B"). The gas flow rate was set at 1.5 L/minute (STP), and the space velocity was 90000 IT⁻¹. SCR activity as a function of temperature of the catalyst was determined. After the test of the activity of the fresh catalyst was completed, the catalyst was treated in an air flow at 800°C for 4 hours ("aging" process as used herein), then the SCR activity as a function of temperature of the aged catalyst was tested. See FIG. 3 for experimental results.

Shown in FIG. 3A is NO conversion rate of the relevant catalyst before aging. Shown in FIG. 3B is NO conversion rate of the relevant catalyst after aging. In the drawings: Curves 3-1 and 3—4 are respectively NO conversion rate as a function of temperature of
the \( \text{WO}_3\text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) (\( x = 0.8 \)) pellet catalyst before and after aging. Curves 3-2 and 3-5 are respectively NO conversion rate of the \( \text{WO}_3\text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) (\( x = 0.5 \)) pellet catalyst before and after aging, and Curves 3-3 and 3-6 are respectively NO conversion rate as a function of temperature of the \( \text{WO}_3\text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) (\( x = 0.2 \)) pellet catalyst before and after aging.

[00120] The curves in FIG. 3 clearly indicate that for a fresh catalyst sample, the activity of the catalyst at low temperature (below 350°C) typically improves with an increase in the content of \( \text{CeO}_2 \) in the sample, while its activity at high temperature decreases with an increase in the content of \( \text{CeO}_2 \) in the sample. An explanation of this phenomenon is that with the increase in the content of \( \text{CeO}_2 \) in the second component of the catalyst, more Ce participates in the cycle of oxidation and reduction at the active site, whereby enhancing the activity of the catalyst at low temperature; at high temperature (350°C or higher), with the presence of more cerium oxides, the activity of the catalyst for \( \text{NH}_3 \) oxidation is enhanced, and more \( \text{NH}_3 \) is oxidized by \( \text{O}_2 \) instead of participating in the reaction of reduction of NO, resulting in a decrease in NO conversion rate. After the catalyst is aged, in the range of 175-300°C, the catalytic activity decreases noticeably; in the range of 300—400°C, the tendency of the decline of the activity tends to slow down, while in the range of 400—500°C, the activity is enhanced instead. The change in the activity of the catalyst before and after aging is related to the redox ability of the catalyst surface. Of the 3 aged samples, the catalyst with the \( \text{CeZr} \) mole ratio of 1:1 had the best SCR activity over the entire temperature range. With both the activity and thermal stability of the catalyst taken into comprehensive consideration, it is advantageous that the \( \text{CeZr} \) mole ratio in the second component of the catalyst is about 1:1.

[00121] Example 4

[00122] Preparation of \( \text{WO}_3\text{Ce}_0\text{Zr}_2\text{O}_2 \) pellet catalyst using the process of incipient wet impregnation, and its characterization

[00123] The process used to prepare the second component \( \text{Ce}_0\text{Zr}_2\text{O}_2 \) was the same as in Example 1 mentioned above, but the \( \text{WO}_3\text{Ce}_0\text{Zr}_2\text{O}_2 \) catalyst was synthesized using the process of incipient wet impregnation. The precursor of \( \text{WO}_3 \) was ammonium metatungstate (\( \text{NH}_4\text{WO}_3 \)). First of all, 25 g of \( \text{NH}_4\text{WO}_3 \) was dissolved in deionized water to prepare 100 ml of solution. Next, 6 g of \( \text{Ce}_0\text{Zr}_2\text{O}_2 \) particles of approximately 20—30 mesh were impregnated using the solution mentioned above. The particles after
impregnation were dried at room temperature for 6 hours, and at 120°C for 3 hours, then calcined at 500°C for 2 hours. The loading of WO₃ in WO₃Ce₀.₈Zr₀.₂O₂ was WO₃:

Ce₀.₈Zr₀.₂O₂ = 0.04 (weight ratio). The catalyst of WO₃Ce₀.₈Zr₀.₂O₂ with WO₃:

Ce₀.₈Zr₀.₂O₂ = 0.08 and 0.12 (weight ratio) was prepared after the steps mentioned above were repeated two to three times.

[00124] The assessment of the SCR activity of the WO₃/Ce₀.₈Zr₀.₂O₂ catalyst with a differing WO₃ loading was conducted in the same way as in Example 1. See FIG. 4 for the test results. For comparison, Ce₀.₈Zr₀.₂O₂ without WO₃ loading is also listed in the drawing. In FIG. 4, Curve 4-1 shows NO conversion rate as a function of temperature on the WO₃/Ce₀.₈Zr₀.₂O₂ (WO₃: Ce₀.₈Zr₀.₂O₂ = 0.04) catalyst, Curve 4-2 shows NO conversion rate as a function of temperature on the WO₃/Ce₀.₈Zr₀.₂O₂ (WO₃: Ce₀.₈Zr₀.₂O₂ = 0.08) catalyst, Curve 4-3 shows NO conversion rate as a function of temperature on the WO₃/Ce₀.₈Zr₀.₂O₂ (WO₃: Ce₀.₈Zr₀.₂O₂ = 0.12) catalyst, and Curve 4-A shows NO conversion rate as a function of temperature on the Ce₀.₈Zr₀.₂O₂ support.

[00125] The curves in FIG. 4 indicate that the SCR activity of the independent second component cerium-zirconium composite oxides without being loaded with the first component is relatively low, as NO conversion rate reaches the highest level at 350°C, which is 70%, and when the temperature is below or higher than 350°C, its catalytic activity will drop rapidly in either case. Yet after it is loaded with a certain amount of the first component WO₃, the functional temperature range is greatly widened, and the activity at both low temperature and high temperature is significantly enhanced. Also, with an increase in the content of the first component WO₃, the activity of the catalyst at low temperature (200-250°C) and its activity at high temperature (400-500°C) are further enhanced.

[00126] Example 5

[00127] Preparation of WO₃Ce₀.₈Zr₀.₂O₂ pellet catalyst using the process of incipient wet impregnation, and its characterization.

[00128] The process used to prepare the second component Ce₀.₅Zr₀.₅O₂ was the same as in Example 3 mentioned above. The WO₃/Ce₀.₅Zr₀.₅O₂ catalyst was synthesized using the process of incipient wet impregnation. 4 g of Ce₀.₅Zr₀.₅O₂ particles of approximately 20-30 mesh were impregnated by ammonium metatungstate (NH₄WO₄) solutions at a series of concentrations, to prepare the WO₃/Ce₀.₅Zr₀.₅O₂ catalyst with different WO₃ loadings. The particles after impregnation were dried at room temperature for 6 hours,
and at 120°C for 3 hours, and then calcined at 500°C for 2 hours. The WO₃ loading in the WO₃Ce₀.₅Zr₀.₅O₂ catalyst was WO₃:Ce₀.₅Zr₀.₅O₂ = 0.065; 0.108, and 0.16 (weight ratio).

[00129] An assessment was made of the SCR activity of the fresh catalyst and the catalyst aged in an 800°C air flow for 1 hour. In the tests, 1 ml of the catalyst of approximately 20-30 mesh was used; a programmed heating reaction process was used, the heating rate was 2 K/min, and the feedstock gas was the Feedstock Gas B as mentioned above. The gas flow was set at 1.5 L/min (STP), and the space velocity was 90000 h⁻¹. See FIG. 5 for the test results. Shown in FIG. 5A is NO conversion rate of the relevant catalyst before aging. Shown in FIG. 5B is NO conversion rate of the relevant catalyst after aging. In the Curves 5-1 and 5-4 are respectively NO conversion rate as a function of temperature of the WO₃Ce₀.₅Zr₀.₅O₂ (WO₃:Ce₀.₅Zr₀.₅O₂ = 0.16) pellet catalyst before and after aging, Curves 5-2 and 5-5 are respectively NO conversion rate as a function of temperature of the WO₃Ce₀.₅Zr₀.₅O₂ (WO₃:Ce₀.₅Zr₀.₅O₂ = 0.108) pellet catalyst before and after aging, and Curves 5-3 and 5-6 are respectively NO conversion rate as a function of temperature of the WO₃Ce₀.₅Zr₀.₅O₂ (WO₃:Ce₀.₅Zr₀.₅O₂ = 0.065) pellet catalyst before and after aging.

[00130] The curves in FIG. 5 clearly indicate that for a fresh catalyst sample, the activity of the catalyst is enhanced with an increase in the content of the first component WO₃, which is in agreement with the results obtained in the example above. However, for an aged catalyst sample, too high WO₃ loading will result in an appreciable drop in the thermal stability of the catalyst. Over the entire temperature range, the catalytic activity of the catalyst with the WO₃ loading of WO₃:Ce₀.₅Zr₀.₅O₂ = 0.108 is consistently higher than the catalyst with the WO₃ loading of WO₃:Ce₀.₅Zr₀.₅O₂ = 0.16. Taking the activity and thermal stability of the catalyst into comprehensive consideration, it is advantageous that the content of WO₃ in the first component of the catalyst be approximately 10% (weight percentage).

[00131] Example 6
[00132] Preparation of WO₃CeₓTiₐₓO₂ pellet catalyst using the process of incipient wet impregnation, and its characterization

[00133] The composite oxides of the second component CeₓTi₁ₓO₂ (x = 0.02; 0.2; 0.25; 0.5) were prepared using the following process. Aqueous solutions of Ce(NO₃)₃ and Ti(SO₄)₄ of 2 mol/L were prepared. 2000 ml of a solution with the total cation
concentration of 0.1 mol/L was prepared from a certain amount of the Ce(NO₃)₃ solution and Ti(SO₄)₄ solution prepared as mentioned above, along with urea and deionized water, with the mole ratio Ce³⁺:Ti⁴⁺:urea = x:(1 - x):15 (x = 0.02; 0.2; 0.25; 0.5). With stirring, said solution was heated to its boiling point, until the precipitate formed. The mixture obtained was then aged at the boiling point for 2 hours, then stirred at room temperature for 2 hours. The precipitate was filtered, then washed with stirring using deionized water for 15 minutes. This step was repeated three times. The filter cake was then eluted with isopropanol using a Buchner funnel. After excess isopropanol was removed through filtering, the precipitate obtained was placed in a vacuum oven dryer, where it was dried at 60°C for approximately 15 hours. The dried precipitate was then calcined at 500°C in a furnace for 2 hours, so that it decomposed to form a CeₓTi₁₋ₓO₂ oxide.

The WO₃ZCeₓTi₁₋ₓO₂ (x = 0.02; 0.2; 0.25; 0.5) catalyst was synthesized using the process of incipient wet impregnation. The precursor of WO₃ was ammonium metatungstate (NH₄WO₄). First of all, 25 g of NH₄WO₄ was dissolved in deionized water to prepare 100 ml of solution. Next, 6 g of CeₓTi₁₋ₓO₂ particles of approximately 20-30 mesh were impregnated using the solution mentioned above. The particles after impregnation were dried at room temperature for 6 hours, and at 120°C for 3 hours, then calcined at 500°C for 2 hours. The WO₃ loading was WO₃:CeₓTi₁₋ₓO₂ = 0.08 (weight ratio).

The assessment of the SCR activity of the WO₃ZCeₓTi₁₋ₓO₂ catalyst for the catalytic NH₃ reduction of NO was conducted in the same way as in Example 1. See FIG. 6 for the test results. In the drawing, Curve 6-1 shows NO conversion rate as a function of temperature on the WO₃ZCeₓTi₁₋ₓO₂ catalyst (x = 0.02), Curve 6-2 shows NO conversion rate as a function of temperature on the WO₃ZCeₓTi₁₋ₓO₂ catalyst (x = 0.2), Curve 6-3 shows NO conversion rate as a function of temperature on the WO₃ZCeₓTi₁₋ₓO₂ catalyst (x = 0.25), and Curve 6-4 shows NO conversion rate as a function of temperature on the WO₃ZCeₓTi₁₋ₓO₂ catalyst (x = 0.5).

The curves in FIG. 6 indicate that by using a Ce-Ti composite oxide as the second component of the catalyst, the catalyst has very good SCR activity when the CeZTi mole ratio is from 1:4 to 1:3. However, when the content of CeO₂ in the catalyst is too high, for example, when the CeZTi mole ratio is 1:1, the activity of the catalyst drops appreciably.
Example 7
Preparation of \( \theta \) \( y \) Ce \( n \) \( s \) Zrn \( s \) \( \theta \) 2 pellet catalyst using the process of incipient wet impregnation, and characterization of the performance after aging with respect to NO \(_2\)ZNO mixture.

The process used to prepare the \( \text{WO}_3\text{Ce}_5\text{Zr}_0\text{S}_2\text{O}_2 \) catalyst was the same as in Example 3.

An assessment was made of the SCR activity of the \( \text{WO}_3\text{ZCe}_0\text{Zr}_0\text{O}_2 \) catalyst aged by an 800 °C air stream for 1 hour using a quartz fixed-bed reactor. To the feedstock gas was added NO \(_2\) at given proportions to observe the NH \(_3\) reduction of \( \text{NO}_x(\text{NO}+\text{NO}_2) \) on the catalyst when NO and NO \(_2\) were both present. The composition of the feedstock gas was: 550 ppm NO \(_x\) (NO + NO \(_2\)), 550 ppm NH \(_3\), 6% O \(_2\), 10% CO \(_2\), 10% H \(_2\)O, and balance N \(_2\), wherein the concentration ratio of NO and NO \(_2\) was set respectively at NO:NO \(_2\) = 3:1, NO:NO \(_2\) = 2:1, and NO:NO \(_2\) = 1:1. The gas flow rate was set at 1.5 LZ/min (STP), and the space velocity was set at 90000 tf \(^{-1}\). The SCR activity as a function of temperature of the catalyst was tested. See FIG. 7 for the test results. In the drawing: Curve 7-1 shows NO conversion rate as a function of temperature, after the \( \text{WO}_3\text{ZCe}_0\text{Zr}_0\text{S}_2\text{O}_2 \) catalyst is aged, with the concentration ratio between NO and NO \(_2\) in the feedstock gas being 1:1; Curve 7-2 shows NO conversion rate as a function of temperature, after the \( \text{WO}_3\text{ZCe}_0\text{Zr}_0\text{S}_2\text{O}_2 \) catalyst is aged, with the concentration ratio between NO and NO \(_2\) in the feedstock gas being 2:1; and Curve 7-3 shows NO conversion rate as a function of temperature, after the \( \text{WO}_3\text{ZCe}_0\text{Zr}_0\text{S}_2\text{O}_2 \) catalyst is aged, with the concentration ratio between NO and NO \(_2\) in the feedstock gas being 3:1.

The curves in FIG. 7 indicate that after the feedstock gas is added with a certain amount of NO \(_2\), the catalytic activity of the aged catalyst is greatly enhanced, particularly in the low temperature range (175-250 °C), and with the increase in the percentage of NO \(_2\), the general NO \(_x\) conversion rate is enhanced; particularly when NO:NO \(_2\) = 1:1, it reaches the optimum reaction performance. It is believed that with the presence of NO \(_2\), the SCR reaction proceeds along the "fast track", which is illustrated by the following equation:

\[ 2\text{NO} + 2\text{NO}_2 + 4\text{NH}_3 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}. \]

Example 8
Preparation of \( \text{WOyCe}_0\text{Zr}_0\text{S}_2\text{O}_2 \) pellet catalyst using the process of solution combustion synthesis, and characterization of its performance before and after aging.

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26.1 g of Ce(NO$_3$)$_3$-6H$_2$O, 60 ml of a 1 mol/L Zr(NO$_3$)$_4$ solution, 5.22 g of urea, 2.0824 g of ammonium metatungstate (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$.H$_2$O), and 100 ml of deionized water were mixed and stirred homogeneously in a 500-ml evaporation dish, then placed in a muffle furnace with the temperature set constant at 500°C. 75 minutes later, the muffle furnace was turned off; when the furnace had cooled to below 200°C, the evaporation dish was taken out and a foam-like catalyst sample was obtained. The sample was calcined, then ground, and passed through a 200-mesh sieve, with the catalyst powder being obtained. The catalyst powder was pressed and shaped, ground, and crushed, and particles of approximately 20—30 mesh were selected through screening for the assessment test. In accordance with this formulation, the Ce/Zr mole ratio in the catalyst is 1:1, and WO$_3$ Ce$_{0.5}$Zr$_{0.5}$O$_2$ = 1:10 (weight ratio).

An assessment was made of the SCR activity of this catalyst for the catalytic NH$_3$ reduction of NO using a quartz fixed-bed reactor. 1 ml of the catalyst of approximately 20-30 mesh was used, and the composition of the feedstock gas was that of Feedstock Gas B. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 90000 h$^{-1}$. The SCR activity as a function of temperature of the catalyst was tested. See FIG. 8 for experimental results. For comparison, the SCR activity as a function of temperature of the catalyst not treated by an air stream is also shown in FIG. 8 as curve 8-1. Curve 8-2 shows NO conversion rate as a function of temperature of the catalyst treated by a 600°C air stream for 4 hours; Curve 8-3 shows NO conversion rate as a function of temperature of the catalyst treated by a 650°C air stream for 4 hours; and Curve 8-4 shows NO conversion rate as a function of temperature of the catalyst treated by a 700°C air stream for 4 hours.

The curves in FIG. 8 clearly show that the WO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst prepared by using the solution combustion synthesis of the present invention has very good SCR activities. The catalyst not having been calcined exhibited relatively lower activity. The catalyst treated at 600°C, 650°C and 700°C had improved activity in the full functional temperature range, particularly in the lower range (<250°C) and higher range (>500°C) where the improvement was appreciable. Among all catalysts subjected to the three calcination temperatures, the one calcined at 700°C showed the best performance in lower temperature range (<250°C) and higher temperature range (>500°C).
Example 9

Preparation of MoO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ pellet catalyst using the process of impregnation, and characterization of its performance before and after aging

The process used to prepare the second component, Ce$_{0.5}$Zr$_{0.5}$O$_2$, was the same as in Example 3 mentioned above. The MoO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst was synthesized using the process of impregnation. First of all, with stirring, 15 g of Ce$_{0.5}$Zr$_{0.5}$O$_2$ powder was mixed and suspended in 50 ml of deionized water. Next, 1.42 g of ammonium molybdate (NFLt$_1$Mo$_7$O$_{24}$·4H$_2$O) was added to the suspension mentioned above, then the mixture obtained was heated in an oil bath to 850°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer, where it was dried at 1200°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a MoO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst of MoO$_3$:$\text{Ce}_0\text{Zr}_0\text{O}_2$ = 1:10 (weight ratio) was obtained. The powder was pressed, then ground, and those particles of 20-30 mesh were selected through screening.

An assessment was made of the SCR activity as a function of temperature of the fresh MoO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst and that of the catalyst aged for 1 hour in an 800°C air flow using a quartz fixed-bed reactor. 1 ml of the catalyst of approximately 20-30 mesh was used, and the composition of the feedstock gas was that of Feedstock Gas B. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 90000 h$^{-1}$. See FIG. 9 for the test results. In the drawing, Curve 9-1 shows NO conversion rate as a function of temperature of the MoO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst before aging. Curve 9-2 shows NO conversion rate as a function of temperature of the MoO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst after aging.

The curves of FIG. 9 indicate that the fresh MoO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst has a very good catalytic activity, particularly in the low temperature range of 175-250 °C, and its activity is higher than the WO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst (WO$_3$:$\text{Ce}_0\text{Zr}_0\text{O}_2$ = 1:10). After aging, the activity of the catalyst drops appreciably and is lower than that of the WO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst (WO$_3$:$\text{WO}_3\text{Ce}_0\text{Zr}_0\text{O}_2$ = 1:10). The melting point of MoO$_3$ is much lower than the melting point of WO$_3$, but the thermal stability of the MoO$_3$/$\text{Ce}_0\text{Zr}_0\text{O}_2$ catalyst is relatively poor.
The process used to prepare the second component Ce$_{0.5}$Zr$_{0.5}$O$_2$ was the same as in Example 3 mentioned above. The CKVCeo$_2$Zr$_2$O$_2$ catalyst was synthesized using the process of impregnation. First of all, with stirring, 10 g of Ce$_{0.5}$Zr$_{0.5}$O$_2$ powder was mixed and suspended in 50 ml of deionized water. Next, 1.6578 g of ammonium dichromate ((NH$_4$)$_2$Cr$_2$O$_7$) was added to the suspension mentioned above, then the mixture obtained was heated in an oil bath to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer, where it was dried at 120°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a CrO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst of CrO$_3$:Ce$_{0.5}$Zr$_{0.5}$O$_2$ = 1:10 (weight ratio) was obtained. The powder was pressed, then ground, and those particles of 20–30 mesh were selected for screening.

An assessment was made of the SCR activity as a function of temperature of the fresh CrO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst and that of the catalyst aged for 1 hour in an 800°C air flow using a quartz fixed-bed reactor. 1 ml of the catalyst of approximately 20-30 mesh was used, and the composition of the feedstock gas was that of Feedstock Gas B. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 90000 h$^{-1}$. See FIG. 10 for the test results. In the drawing, Curve 10-1 shows NO conversion rate as a function of temperature of the CrO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst before aging. Curve 10-2 shows NO conversion rate as a function of temperature of the CrO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst after aging.

The curves of FIG. 10 indicate that the fresh CrO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst shows good catalytic activity in the temperature range of 175-300°C, and at 250°C it reaches the highest NO conversion rate, which is 89%. When the temperature is higher than 300°C, NO conversion rate drops rapidly. The rapid drop in the activity of the catalyst at high temperature is related to a stronger oxidation ability of CrO$_3$, as a result of which more NH$_3$ is oxidized by O$_2$ instead of participating in the reduction reaction of NO; also, the product of the oxidation of NH$_3$ contains a certain amount of NO$_x$. After aging, the performance of the CrO$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst is further attenuated.

Example 11

Preparation of Fe$_2$O$_3$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ pellet catalyst using the process of impregnation and characterization of its performance before and after aging.
The process used to prepare the second component \( \text{Ce}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) was the same as in Example 3 mentioned above. The \( \text{Fe}_2 \cdot \text{O}_3 \cdot \text{ZCe}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) catalyst was synthesized using the process of impregnation. First of all, with stirring, 10 g of \( \text{Ce}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) powder was mixed and suspended in 50 ml of deionized water. Next, 5.05 g of ferrous nitrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O) was added to the suspension mentioned above, then the mixture obtained was heated in an oil bath to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer, where it was dried at 120°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a \( \text{Fe}_2 \cdot \text{O}_3 \cdot \text{ZCe}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) catalyst \( \text{FeFe}_2 \cdot \text{O}_3 \cdot \text{Ce}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 = 1:10 \) (weight ratio) was obtained. The powder was pressed, then ground, and those particles of 20-30 mesh were selected through screening.

An assessment was made of the SCR activity as a function of temperature of the fresh \( \text{Fe}_2 \cdot \text{O}_3 \cdot \text{ZCe}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) catalyst and that of the catalyst aged for 1 hour in an 800°C air flow using a quartz fixed-bed reactor. 1 ml of the catalyst of approximately 20-30 mesh was used, and the composition of the feedstock gas was that of Feedstock Gas B. The gas flow rate was set at 1.5 LZ/min (STP), and the space velocity was set at 90000 h\(^{-1}\). See FIG. 11 for the test results, hi the drawing. Curve 11-1 shows NO conversion rate as a function of temperature of the \( \text{Fe}_2 \cdot \text{O}_3 \cdot \text{ZCe}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) catalyst before aging. Curve 11-2 shows NO conversion rate as a function of temperature of the \( \text{Fe}_2 \cdot \text{O}_3 \cdot \text{ZCe}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) catalyst after aging.

The curves of FIG. 11 indicate that the fresh \( \text{Fe}_2 \cdot \text{O}_3 \cdot \text{ZCe}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) catalyst shows a certain SCR activity, and at 350°C it reaches the highest NO conversion rate, which is 45%. After aging, the performance of the \( \text{Fe}_2 \cdot \text{O}_3 \cdot \text{ZCe}_0 \cdot \text{Zr}_{0.5} \cdot \text{O}_2 \) catalyst is further attenuated.
the mixture obtained was heated in an oil bath to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer, where it was dried at 120°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a MnO₆/Co₅Zr₅O₂ catalyst of MnO₆: Co₅Zr₅O₂ = 1:10 (weight ratio) was obtained. The powder was pressed, then ground, and those particles of 20-30 mesh were selected through screening.

An assessment was made of the SCR activity as a function of temperature of the fresh MnO₆/Co₅Zr₅O₂ catalyst and that of the catalyst aged for 1 hour in an 800°C air flow using a quartz fixed-bed reactor. 1 ml of the catalyst of approximately 20-30 mesh was used, and the composition of the feedstock gas was Feedstock Gas B. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 90000 h⁻¹. See FIG. 12 for the test results. In the drawing, Curve 12-1 shows NO conversion rate as a function of temperature of the MnO₆/Co₅Zr₅O₂ catalyst before aging. Curve 12-2 shows NO conversion rate as a function of temperature of the MnO₆ZCe₀.₅Zr₀.₅O₂ catalyst after aging.

The curves of FIG. 12 indicate that the fresh MnO₆ZCe₀.₅Zr₀.₅O₂ catalyst shows a certain catalytic activity; at 350°C, it reaches the highest NO conversion rate, which is 61%. After aging, the performance of the MnO₆ZCe₀.₅Zr₀.₅O₂ catalyst is further attenuated.

Example 13

Preparation of V₂O₅ZCe₀.₅Zr₀.₅O₂ pellet catalyst using the process of impregnation, and characterization of its performance before and after aging.

The process used to prepare the second component, Ce₀.₅Zr₀.₅O₂, was the same as in Example 3 mentioned above. The V₂O₅ZCe₀.₅Zr₀.₅O₂ catalyst was synthesized using the process of impregnation. First of all, a solution of the mixture of ammonium metavanadate and oxalic acid was prepared. 2.7 g of ammonium metavanadate (NH₄VO₃) and 5.4 g of oxalic acid were dissolved in a certain amount of deionized water and heated until boiling; later, a dark blue solution was formed. The solution mentioned above was cooled and set at a constant volume of 50 ml. With stirring, 10 g of Ce₀.₅Zr₀.₅O₂ powder was mixed and suspended in 40 ml of deionized water. Next, 12 ml of the solution that contained chemical compounds of vanadium prepared above was added to the suspension mentioned above, then the mixture obtained was heated in an oil
bath to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer, where it was dried at 120°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a V_2O_5/Ce_0.5Zr_0.5O_2 catalyst of V_2O_5:Ce_0.5Zr_0.5O_2 = 1:20 (weight ratio) was obtained. The powder was pressed, then ground, and those particles of 20-30 mesh were selected through screening.

An assessment was made of the SCR activity as a function of temperature of the fresh V_2O_5/Ce_0.5Zr_0.5O_2 catalyst and that of the catalyst aged for 1 hour in an 800°C air flow using a quartz fixed-bed reactor. 1 ml of the catalyst of approximately 20-30 mesh was used, and the composition of the feedstock gas was that of Feedstock Gas B. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 90000 h\(^{-1}\). See FIG. 13 for the test results. In the drawing, Curve 13-1 shows NO conversion rate as a function of temperature of the V_2O_5/Ce_0.5Zr_0.5O_2 catalyst before aging. Curve 13-2 shows NO conversion rate as a function of temperature of the V_2O_5/Ce_0.5Zr_0.5O_2 catalyst after aging.

The curves of FIG. 13 indicate that the fresh V_2O_5/Ce_0.5Zr_0.5O_2 catalyst shows a certain catalytic activity; at 350°C, it reaches the highest NO conversion rate, which is 61%. After aging, the performance of the V_2O_5/Ce_0.5Zr_0.5O_2 catalyst is further attenuated.

Example 14

Preparation of the structured WOVCe OsZrn2O3 cordierite honeycomb ceramic catalyst, and characterization of its performance

The present example relates to the preparation of a structured catalyst. Cordierite honeycomb of 400 cells/square inch (cells per square inch, cpsi) (made in Shanghai) and cordierite honeycomb of 600 cpsi (made by Corning of the United States) were used as the ceramic support. First of all, the honeycomb cordierite was cut into small cylinders with a size of 0 16 x 25 (mm). The honeycomb ceramic was then washed at room temperature for 3 hours using a 3.0-wt% nitric acid solution. The ceramic was dried in a dryer at 120°C for 10 hours, then calcined at 900°C for 2 hours.

The cerium-zirconium sol sample was prepared as follows: First of all, 434 g of Ce(NO_3)_3·6H_2O was dissolved in a solution of water and 125 ml of a 2 mol/L solution of Zr(NO_3)_4. The solution of the cerium-zirconium mixture was diluted to a volume of 440 ml. With stirring, 90 ml of a 12.5% aqueous ammonia solution was added drop-wise
into the cerium-zirconium solution at the rate of 1.5 seconds per droplet to obtain the cerium-zirconium gel. After that, with stirring, 50 ml of a 2 mol/L solution of nitric acid was added to the gel at a rate of 5 seconds per droplet, then the mixture was stirred for 8 hours, and the cerium-zirconium (4:1) sol was obtained.

5 [00176] The honeycomb ceramic after pre-treatment was impregnated using the cerium-zirconium (4:1) sol obtained, then the residual solution in the honeycomb passageway was removed using hot air. After the removal was complete, the sample was dried using a microwave oven for three minutes, then calcined at 500°C for 2 hours in a programmed temperature furnace. For a honeycomb ceramic of 400 cpsi, this step was repeated 4 times; approximately 0.7 g of the cerium-zirconium composite oxide was loaded on the honeycomb ceramic. For a honeycomb ceramic of 600 cpsi, this step was repeated seven times; approximately 0.78 g of the cerium-zirconium composite oxide was loaded on the honeycomb ceramic.

10 [00177] The cerium-zirconium composite oxide/cordierite honeycomb ceramic was then impregnated using an ammonium metatungstate (NH₄WO₄) solution (100 ml of the solution was prepared from 25 g of NH₄WO₄ dissolved in deionized water), then the residual solution in the honeycomb passageway was removed using hot air. After the removal was complete, the sample was dried using a microwave rapid drying machine, then calcined at 500°C for 2 hours in a programmed temperature furnace.

15 [00178] An assessment was made of the SCR activity of the WO₃/Co₃Zr₁₋₂O₂/cordierite catalyst using the quartz fixed-bed reactor. The feedstock gas was that of Feedstock Gas A... The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 22500 h⁻¹. See FIG. 14 for the test results. In the drawing, Curve 14—1 shows NO conversion rate as a function of temperature of the WO₃/Co₃Zr₁₋₂O₂/cordierite honeycomb ceramic catalyst with a 400 cpsi cell density; Curve 14—2 shows NO conversion rate as a function of temperature of the WO₃/ZrCe₈/2O₂/cordierite honeycomb ceramic catalyst with a 600 cpsi cell density.

20 [00179] The curves in FIG. 14 indicate that the WO₃/ZrCe₈/2O₂/cordierite honeycomb ceramic catalyst prepared with cerium-zirconium sol as the cerium-zirconium precursor has a very good SCR catalytic activity. The higher the cell density of the honeycomb ceramic, the better the active component of the catalyst can be utilized, and the higher its catalytic activity will be.
Example 15

Preparation of the structured WCW\textsubscript{cns}Zr\textsubscript{2}O\textsubscript{2} cordierite honeycomb ceramic catalyst, and characterization of its performance

The present example relates to the preparation of a structured catalyst. A 400 cpsi honeycomb cordierite made in Shanghai was used as the ceramic support. The process of pre-treatment was the same as described in Example 14. A cerium-zirconium slurry was used in place of the cerium-zirconium sol for preparation of the coating of the ceramic. The cerium-zirconium slurry was prepared as follows: 24 g of Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2} powder (the process of preparation was the same as in Example 1), 35 ml of cerium-zirconium (4:1) sol (the process of preparation was the same as in Example 14), and 10 ml of nitric acid (pH = 1.2) were mixed. The mixture was ground by means of the wet ball milling process for 18 hours and the cerium-zirconium slurry was obtained.

The honeycomb ceramic after pre-treatment was impregnated using the cerium-zirconium slurry obtained, then the residual sol or slurry in the honeycomb passageway was removed using hot air. After the removal was complete, the sample was dried using a microwave rapid drying machine, then calcined at 500°C for 2 hours in a programmed temperature furnace. This step was repeated six times, so that approximately 0.77 g of the cerium-zirconium composite oxide was loaded onto the honeycomb ceramic.

The cerium-zirconium composite oxide/cordierite honeycomb ceramic was then impregnated using an ammonium metatungstate (NH\textsubscript{4}WO\textsubscript{3}) solution (100 ml of the solution was prepared from 25 g of NH\textsubscript{4}WO\textsubscript{3} dissolved in deionized water), then the residual solution in the honeycomb passageway was removed using hot air. After the removal was complete, the sample was dried using a microwave rapid drying machine, then calcined at 500°C for 2 hours in a programmed temperature furnace.

An assessment was made of the SCR activity of the WO\textsubscript{3}/Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2}/cordierite catalyst using the quartz fixed-bed reactor. The feedstock gas was Feedstock Gas A. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 22500 h\textsuperscript{-1}. See FIG. 15 for the test results.

The curves in FIG. 15 indicate that the WO\textsubscript{3}/Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2}/cordierite honeycomb ceramic catalyst prepared with cerium-zirconium slurry as the cerium-zirconium precursor also has a very good SCR catalytic activity.

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Example 16

Preparation of the structured WO$_3$/Ce$_{0.8}$Zr$_{0.2}$O$_2$ cordierite honeycomb ceramic catalyst, and characterization of its performance

The present example relates to the preparation of a structured catalyst. The cerium-zirconium slurry was used for preparation of the catalytic coating. In the present example, the cerium-zirconium slurry was prepared from Ce$_{0.5}$Zr$_{0.5}$O$_2$ powder prepared using the microemulsion process. The process used to prepare the Ce$_{0.5}$Zr$_{0.5}$O$_2$ powder was as follows: Step 1—43.42 g of cerium nitrate and 42.92 g of zirconium nitrate were dissolved using deionized water and the concentration was set to 1 mol/L; also, 25 ml of a 25-wt% aqueous ammonia solution was diluted to 50 ml, and a 7.5M aqueous ammonia solution was obtained. Step 2—production of the microemulsion. First, 100 ml of polyoxyethylene (10) octylphenyl ether (hereinafter "Np-10") and 120 ml of n-hexanol were added at room temperature and under stirring to 400 ml of n-hexane, until the solution mixture became clear. The Ce(NO$_3$)$_3$ and Zr(NO$_3$)$_4$ solution obtained in Step 1 was then added to the solution mixture, and stirred, until the mixture solution became clear again. Another emulsion in which 50 ml of the aqueous ammonia solution obtained in Step 1 was dissolved was prepared using the same technique mentioned above. Step 3—the two kinds of microemulsions with different concentration levels were mixed in a 2000 ml beaker. The mixture was reacted, with stirring, for half an hour, then the microparticles were separated through reflux and vacuum dried at 70°C for 12 hours. The dried sample was calcined at 500°C in a muffle furnace for 2 hours. As a result, approximately 12 g of an extremely fine powder of cerium-zirconium composite oxide was obtained.

12 g of the powder of Ce$_{0.5}$Zr$_{0.5}$O$_2$ oxide prepared using the microemulsion process, 17 ml of the cerium-zirconium sol with a 1:1 mole ratio prepared under the same conditions as described in Example 14, 5 ml of nitric acid (pH = 1.2), and 10 ml of deionized water were ground by means of the wet ball milling process for 20 minutes; the Ce$_{0.5}$Zr$_{0.5}$O$_2$ slurry was obtained.

The 400 cpsi honeycomb ceramic after pre-treatment was impregnated using the Ce$_{0.5}$Zr$_{0.5}$O$_2$ slurry obtained, then the residual sol or slurry in the honeycomb passageway was removed using hot air. After the removal was complete, the sample was dried using a microwave rapid drying machine, then calcined at 500°C for 2 hours in a programmed temperature furnace. This step was repeated for several times, so that
approximately 0.6358 g and 0.4165 g of the cerium-zirconium composite oxides were respectively loaded onto the honeycomb ceramic.

[00192] The cerium-zirconium composite oxide/cordierite honeycomb ceramic was then impregnated using an ammonium metatungstate (NH₄WO₃) solution (100 ml of the solution was prepared from 25 g of NH₄WO₃ dissolved in deionized water), then the residual solution in the honeycomb passageway was removed using hot air. After the removal was complete, the sample was dried using a microwave rapid drying machine, then calcined at 500°C for 2 hours in a programmed temperature furnace.

[00193] An assessment was made of the SCR activity of the W₀/₃CeO₂Zr₀₅O₂/cordierite catalyst using the quartz fixed-bed reactor. A reaction under programmed heating was carried out; the heating rate was 2 K/min and the feedstock gas was Feedstock Gas B. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 22500 h⁻¹. See FIG. 16 for the test results. In the drawing, Curve 16—1 is NO conversion rate as a function of temperature of the W₀/₃CeO₂Zr₀₅O₂/cordierite honeycomb ceramic catalyst when the Ce₀₅Zr₀₅O₂ loading is 0.6358 g; Curve 16-2 is NO conversion rate as a function of temperature of the W₀/₃CeO₂Zr₀₅O₂/cordierite honeycomb ceramic catalyst with a 0.4165 g Ce₀₅Zr₀₅O₂ loading.

[00194] The curves of FIG. 16 indicate that the honeycomb ceramic catalyst with the cerium-zirconium composite oxide prepared using the microemulsion process as the second component, even when the loading of the cerium-zirconium composite oxide is only 0.4165, shows a very high SCR reaction activity. With the loading of the cerium-zirconium composite oxide increased to 0.6358 g, NO conversion rate of the catalyst is further enhanced; at 300^450 0°C, NO conversion rate is higher than 90%, and up to 98%.

[00195] Example 17

[00196] Preparation of the structured W₀/₃yCeO₂Zr₀₅O₂/cordierite honeycomb ceramic catalyst, and characterization of its performance

[00197] The present example relates to the preparation of an structured catalyst. First of all, the W₀/₃CeO₂Zr₀₅O₂ powder was synthesized using the process of impregnation. With stirring, 12 g of Ce₀₅Zr₀₅O₂ powder (the process of preparation is the same as in Example 3) was mixed and suspended in 50 ml of deionized water. Next, 1.41 17 g of ammonium metatungstate (NH₄WO₃) was added to the suspension mentioned above, and the mixture obtained was heated in an oil bath to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was
transferred to a dryer, where it was dried at 120°C overnight. The dried sample was calcined at 500°C for 2 hours, and a \( \text{WO}_3/\text{Ce}_0.5\text{Zr}_0.5\text{O}_2 \) slurry of \( \text{WO}_3: \text{Ce}_x \text{Zr}_{1-x} \text{O}_2 = 1:10 \) (weight ratio) was obtained.

[00198] 12 g of the powder \( \text{OfWO}_3\text{ZrCe}_0.5\text{Zr}_0.5\text{O}_2 \) oxide, 17 ml of the cerium-zirconium sol with a 1:1 mole ratio prepared under the same technological conditions as described in Example 14, and 10 ml of nitric acid (pH = 1.2) were ground by means of the wet ball milling process for 18 hours, and the \( \text{WO}_3/\text{Ce}_0.5\text{Zr}_0.5\text{O}_2 \) slurry was obtained.

[00199] The 400 cpsi honeycomb ceramic after pre-treatment was impregnated using the \( \text{WO}_3/\text{Ce}_0.5\text{Zr}_0.5\text{O}_2 \) slurry obtained, then the residual sol or slurry in the honeycomb passageway was removed using hot air. After the removal was complete, the sample was dried using a microwave rapid drying machine, then calcined at 500°C for 2 hours in a programmed temperature furnace. This step was repeated for 4 times, so that approximately 0.881 g of \( \text{WO}_3/\text{Ce}_0.5\text{Zr}_0.5\text{O}_2 \) was loaded onto the honeycomb ceramic.

[00200] The assessment of the SCR activity of the \( \text{WO}_3/\text{Ce}_0.5\text{Zr}_0.5\text{O}_2 \)/cordierite catalyst was the same as Example 13. The gas flow rate was set at 1.5 L/min (STP), and the space velocity was set at 22500 h⁻¹. See FIG. 17 for the test results.

[00201] The curves of FIG. 16 indicate that the \( \text{WO}_3/\text{Ce}_0.5\text{Zr}_0.5\text{O}_2 \)/honeycomb ceramic catalyst with the cerium-zirconium composite oxide prepared using said process also has a very good SCR activity. Therefore, \( \text{WO}_3 \) may be loaded onto the honeycomb ceramic catalysts in different ways.

[00202] Example 18 (comparative example)

[00203] Preparation of a catalyst in the prior art according to a prior art process

[00204] In the present example, using the process disclosed in Column 9 of U.S. Patent No. 5,552,128, Catalyst B disclosed in the same column of said patent was prepared, and its performance was assessed and characterized. The specific process was as follows.

[00205] In a beaker, 50 g of \( \text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} \) and 0.36 g of \( \text{Ce(SO}_4)_2 \) were dissolved in 700 ml of deionized water, to prepared a Solution AAl; 5.4 g of ammonium metatungstate \( ((\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40})\cdot\text{XH}_2\text{O}) \) was dissolved in 26.3 g of concentrated aqueous ammonia (mass concentration 25%), with 50 ml of deionized water being added, whereby a Solution BBl was prepared, which was then placed in a separatory funnel. With stirring, Solution BBl was added drop-wise into the beaker containing Solution AAl, with a controlled and monitored addition rate so that the addition process was
complete within 30-40 minutes. After the addition was complete, a certain amount of concentrated aqueous ammonia (mass concentration 25%) was added to the beaker, to adjust the pH value of the mixture to approximately 9. The mixture obtained was then transferred to a three-neck flask, where it was aged in a 100°C oil bath for 72 hours.

After the aging was complete, the mixture was filtered so that the precipitate was separated from the mother liquor, then the precipitate was washed with stirring using 100°C hot water for 20 minutes. It was thoroughly washed 3 times; after each washing, the solid and liquid were separated by means of filtering. After washing was complete, the filter cake was put into an 85°C oven dryer where it was dried for 12 hours, then transferred to a muffle furnace where it was calcined at 825°C for 3 hours. After the calcined sample was ground, it was screened with a 200-mesh sieve, and the catalyst powder was obtained. The catalyst powder was pressed and shaped, ground, and crushed, then particles of 20-30 mesh were selected through screening for the assessment tests. The assessment tests were conducted once under the following two conditions (Condition A, Condition B) respectively.

[00206] Condition A (the following data on the composition are volume percentages and volume fractions):

[00207] Composition of the feedstock gas: 500 ppm NO, 500 ppm NH₃, and 1% O₂, and balance N₂.

[00208] Space velocity: 800000 hr⁻¹.

[00209] For the result of the assessment under Condition A, see FIG. 18. In the drawing, Curve 18-1 shows the results of assessment of the catalyst of the present example.

[00210] Condition B (the following data on the composition included the volume percentage and volume fraction):

[00211] Composition of the feedstock gas: 550 ppm NO, 550 ppm NH₃, 10% H₂O, 10% CO₂, 6% O₂, and balance N₂;

[00212] Space velocity: 900000 hr⁻¹.

[00213] For the results of the assessment under Condition B, see FIG. 19. In the drawing, Curve 19-1 shows the results of assessment of the catalyst of the present example.
Example 19

Preparation of the catalyst according to certain embodiments of the present invention using a process similar to that in the prior art.

In the present example, a catalyst with the chemical composition of the present invention was prepared using the process disclosed in Column 9 of U.S. Patent No. 5,552,128 for Catalyst B disclosed therein; its performance was tested and characterized. Compared with Catalyst B disclosed in Column 9 of U.S. Patent No. 5,552,128, the catalyst prepared in the present example had an even higher content of cerium. The specific process of preparation was as follows:

In a beaker, 25 g of ZrOCl₂·8H₂O and 42.5 g of (NH₄)₂Ce(NO₃)₆ were dissolved in 700 ml of deionized water, forming Solution AA2; 2.69 g of ammonium metatungstate (NH₄)₂O₂W₂O₇·xH₂O) was dissolved in 26.3 g of concentrated aqueous ammonia (mass concentration 25%), then 50 ml of deionized water was added for it to be diluted, to form a Solution BB2 was prepared, which was placed in a separatory funnel. With stirring, Solution BB2 was added drop-wise into the beaker containing Solution AA2, with a controlled addition rate such that the addition process was complete within 30-40 minutes. After the addition was complete, a certain amount of concentrated aqueous ammonia (mass concentration 25%) was added to the beaker, to adjust the pH value of the mixture to approximately 9. The mixture obtained was then transferred to a three-neck flask to be aged in a 100°C oil bath for 72 hours. After the aging was complete, the mixture was filtered so that the precipitate was separated from the mother liquor, and the precipitate was washed with stirring using 100°C hot water for 20 minutes. It was thoroughly washed 3 times; after each washing, the solid and liquid were separated by filtering. After washing was complete, the filter cake was put into an 85°C oven dryer where it was dried for 12 hours, then transferred to a muffle furnace where it was calcined at 825°C for 3 hours. After the calcined sample was ground, it was screened with a 200-mesh sieve and the catalyst powder was obtained. The catalyst powder was pressed and shaped, ground, and crushed, and particles of 20—30 mesh were selected through screening for the assessment tests. The assessment tests were conducted once respectively under Condition A and Condition B as described in Example 18. For the results of the assessment under Condition A, see FIG. 18. In the drawing, Curve 18-2 shows the results of the assessment of the catalyst of the present example. For the results of the assessment under Condition B, see FIG. 19. In the
drawing, Curve 19-2 shows the results of the assessment of the catalyst of the present example.

Example 20  Preparation of the catalyst of certain embodiments of the present invention

In order to make an effective comparison with Example 18 and Example 19, a catalyst whose chemical composition was the same as that of the catalyst of Example 18 was prepared in the present example using the process of the present invention, and its performance was tested and characterized. The specific method was as follows.

2000 ml of a solution with the cation concentration of 0.1 mol/L was prepared from 54.8 g Of(NIL)\textsubscript{2}Ce(NO\textsubscript{3})\textsubscript{6} and 50 ml of a 2-mol/L Zr(NO\textsubscript{3})\textsubscript{4} solution and deionized water. With stirring, said solution was heated to its boiling point, until the precipitate was observed. The mixture obtained was then aged at the boiling point for 2 hours, then stirred at room temperature for 2 hours. The precipitate was filtered, then washed with stirring using 1500 ml of deionized water for 15 minutes. This step was repeated three times. The filter cake was then eluted with 300 ml of propanol using a Buchner funnel. After excess propanol was removed through filtering, the precipitate obtained was placed in a vacuum oven dryer, where it was dried at 60°C for approximately 15 hours. The dried precipitate was then calcined at 500°C in a furnace for 2 hours, so that it decomposed to form a Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} oxide.

The WO\textsubscript{3}/Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} catalyst was synthesized using the process of impregnation. With stirring, 15 g of Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} powder was mixed and suspended in 50 ml of deionized water. Next, 1.7647 g of ammonium metatungstate (NH\textsubscript{4})\textsubscript{6}H\textsubscript{2}W\textsubscript{12}O\textsubscript{46}·nH\textsubscript{2}O was added to the suspension mentioned above, and the mixture obtained was heated to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer, where it was dried at 120°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a WO\textsubscript{3}/Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} powder of WO\textsubscript{3}: Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} = 1:10 (weight ratio) was obtained. The catalyst powder was pressed and shaped, then ground and crushed, and particles of approximately 20-30 mesh were selected through screening for the assessment tests.

The assessment tests were conducted once respectively under Condition A and Condition B as described in Example 18. For the results of the assessment under
Condition A, see FIG. 18. In the drawing, Curve 18-3 shows the results of the assessment of the catalyst of the present example. For the results of the assessment under Condition B, see FIG. 19. In the drawing, Curve 19-3 shows the results of the assessment of the catalyst of the present example.

5  [00224] Example 21

[00225] Preparation of the catalyst whose chemical composition is the same as the catalyst disclosed by the existing technology using the process in certain embodiments of the present invention

[00226] In the present example, a catalyst whose chemical composition was the same as that of Catalyst B disclosed in Column 9 of U.S. Patent No. 5,552,128 was prepared using the process of impregnation in certain embodiments of the present invention, and its performance was assessed and characterized. The specific process was as follows.

[00227] 2000 ml of solution with the cation concentration of 0.1 mol/L was prepared from 0.65 g (NFLO₂Ce(NO₃)₆ and 100 ml of a 2-mol/L Zr(NO₃)₄ solution along with 180 g of urea added with deionized water. With stirring, said solution was heated to its boiling point, until the precipitate was observed. The mixture obtained was then aged at the boiling point for 2 hours, then stirred at room temperature for 2 hours. The precipitate was filtered, then washed with stirring using 1500 ml of deionized water for 15 minutes. This step was repeated three times. The filter cake was then eluted with 300 ml of propanol using a Buchner funnel. After excess propanol was removed through filtering, the precipitate obtained was placed in a vacuum oven dryer, where it was dried at 60°C for approximately 15 hours. The dried precipitate was then calcined at 500°C in a furnace for 2 hours, so that it decomposed to form an oxide.

[00228] The catalyst was synthesized using the process of impregnation. First of all, with stirring, the oxide powder prepared as mentioned above was mixed and suspended in 50 ml of deionized water. Next 4.41 g of ammonium metatungstate (NFLi)OH₂W₁₂O₄₃·XH₂O) was added to the suspension mentioned above, and the mixture obtained was heated to 85°C. It was heated continuously with stirring, until most of the moisture evaporated, and a paste was obtained. The paste was transferred to a dryer, where it was dried at 120°C for 6 hours. The dried sample was calcined at 500°C for 2 hours, and a catalyst powder was obtained. The catalyst powder was pressed and shaped, then ground and crushed, and particles of approximately 20-30 mesh were selected through screening for the assessment tests.
The assessment tests were conducted once respectively under Condition A and Condition B as described in Example 18. For the results of the assessment under Condition A, see FIG. 18. In the drawing, Curve 18—4 shows the results of the assessment of the catalyst of the present example. For the results of the assessment under Condition B, see FIG. 19. In the drawing, Curve 19—4 shows the results of the assessment of the catalyst of the present example.

The curves in FIG. 18 and FIG. 19 clearly indicate that the catalyst prepared using the process of preparation of the present invention, and that has the chemical composition of the catalyst of the present invention, shows the best catalytic results at a low temperature, while Catalyst B of said patent prepared using the process disclosed in Column 9 of U.S. Patent No. 5,552,128 shows the worst catalytic results at low temperature; also, compared with a catalyst that has the same chemical composition as Catalyst B disclosed in Column 9 of U.S. Patent No. 5,552,128 (whether it is prepared using the process of the present invention or prepared using the process disclosed in U.S. Patent No. 5,552,128), the catalyst that has the chemical composition of the present invention (whether it is prepared using the process of the present invention or prepared using the process disclosed in U.S. Patent No. 5,552,128) consistently has a much better catalytic result at low temperature.

It will be apparent to those skilled in the art that various modifications and alterations can be made to the present invention without departing from the scope and spirit of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.
CLAIMS

1. A catalyst for the selective reduction of a nitrogen oxide, characterized in that it comprises a first component and a second component, wherein:

   the first component is selected from oxides of a transition metal other than the metal contained in the second component, and mixtures and combinations thereof; with the amount of the first component, based on the total weight of the first component and the second component, being from 0.1% to 30%; and

   the second component is selected from (i) cerium oxides, (ii) oxides of lanthanides other than cerium, (iii) composite oxides of cerium and zirconium, (iv) composite oxides of a lanthanide other than cerium and zirconium, (v) composite oxides of cerium and titanium, (vi) composite oxides of a lanthanide other than cerium and titanium, and (vii) combinations and mixtures of two or more of (i), (ii), (iii), (iv), (v) and (vi); with the amount, in moles, of lanthanide atoms in the second component being at least 1% of the total amount, in moles, of the metallic atoms in the second component; and with the amount of the second component, based on oxides of the metal(s) at the highest valency, being from 70% to 99.9% of the total weight of the first component and the second component.

2. A catalyst according to Claim 1, characterized in that the first component is selected from V2O5, MoO3, WO3, and mixtures and combinations thereof.

3. A catalyst according to Claim 2, characterized in that the first component is selected from MoO3,WO3, and mixtures and combinations thereof.

4. A catalyst according to Claim 1, characterized in that the second component is selected from cerium oxides, composite oxides of cerium and zirconium, composite oxides of cerium and titanium, and mixtures and combinations of two or more of these.

5. A catalyst according to Claim 4, characterized in that the second component is a composite oxide of cerium and zirconium.

6. A catalyst according to any one of Claims 1 to 5, characterized in that the amount of the first component is from 5% to 20% of the total weight of the first component and the second component.

7. A catalyst according to any one of Claims 1 to 5, characterized in that the amount of the first component is from 6% to 15% of the total weight of the first component and the second component.
8. A catalyst according to Claim 5, characterized in that the mole ratio of cerium atoms to zirconium atoms in the second component is from 0.01:1 to 10:1.

9. A catalyst according to Claim 8, characterized in that the mole ratio of cerium atoms to zirconium atoms in the second component is from 1:10 to 1:1.

10. A catalyst according to Claim 9, characterized in that the second component is a nanocrystalline material.

11. A catalyst according to any one of Claims 1—5, characterized in that it is in pellet form.

12. A catalyst according to any one of Claims 1-5, characterized in that it further comprises a porous support on which the first component and the second component are loaded.

13. A method for making a catalyst according to Claim 11, characterized in that it comprises:
   (1) forming a precursor of the second component by co-precipitation of an aqueous solution, then calcining the precursor to obtain the second component; and
   (2) loading a precursor of the first component on the second component obtained in step (1).

14. A method according to Claim 13, characterized in that step (1) comprises:
   (IA) providing an aqueous solution of a salt of cerium, a salt of zirconium and urea;
   (IB) co-precipitating the aqueous solutions obtained in step (IA) to obtain a precursor of a composite oxide of cerium and zirconium; and
   (1C) calcining the precursor obtained in step (IB).

15. A method according to Claim 13 or Claim 14, characterized in that step (2) comprises:
   (2A) forming an aqueous dispersion comprising a precursor of the first component and the second component obtained in step (1);
   (2B) evaporating part of the solvent in the aqueous dispersion to obtain a paste; and
   (2C) drying and calcining the paste.

16. A method for making a catalyst according to Claim 11, characterized in that it comprises:
   forming the catalyst by combustion synthesis.
17. A method according to Claim 16, characterized in that it comprises:

(i) providing an aqueous dispersion comprising a salt of cerium, a salt of zirconium, a tungsten-containing salt and urea; and

(ii) heating the aqueous dispersion until it decomposes to obtain a powder; and

(iii) calcining the powder obtained in step (ii) to obtain the catalyst.

18. A method for making catalyst according to claim 17, characterized in that the calcining temperature in step (iii) is from 500 to 700°C.

19. A method for making a catalyst according to Claim 12, characterized in that it comprises:

(I) providing an aqueous dispersion of the second component;

(II) impregnating a porous support with the aqueous dispersion obtained in step (I);

(III) drying and calcining the object treated in step (II);

(IV) impregnating the object treated in step (III) with a liquid dispersion comprising a precursor of the first component; and

(V) drying and calcining the object treated in step (IV).

20. A method according to Claim 19, characterized in that step (I) comprises:

(A) providing an aqueous dispersion comprising a mixture of a salt of cerium and a salt of zirconium;

(B) adding ammonia into the aqueous dispersion obtained in step (IA) until a gel comprising cerium and zirconium is obtained;

(C) adding nitric acid into the gel obtained in step (IB), thereby obtaining a sol comprising cerium and zirconium.

21. A method according to Claim 19, characterized in that step (I) comprises:

(Ia) providing a powder of a composite oxide of cerium and zirconium;

(Ib) providing a sol comprising cerium and zirconium; and

(Ic) mixing nitric acid, the powder obtained in step (Ia) and the sol obtained in step (Ib) and grinding the resulting mixture, thereby obtaining a slurry which is the aqueous dispersion of the second component.

22. A method according to Claim 19, characterized in that step (I) comprises:

(II) providing an aqueous emulsion comprising a surfactant, a co-surfactant, an oil-phase solvent, a salt of cerium and a salt of zirconium;
(12) providing an aqueous emulsion comprising a surfactant, a co-surfactant, an oil-phase solvent, and ammonia;
(13) mixing the aqueous emulsion obtained in step (II) with the aqueous emulsion obtained in step (12);
(14) separating the solid particles formed in step (13) in the aqueous emulsion;
(15) drying and calcining the solid particles obtained from step (14); and
(16) mixing the solid particles obtained in step (15), a sol comprising cerium and zirconium and nitric acid, and grinding the mixture; thereby obtaining a slurry which is the aqueous dispersion of the second component.

23. A method for making a catalyst according to Claim 12, characterized in that it comprises:
(1) providing an aqueous suspension of a composite oxide of cerium and zirconium;
(2) adding a precursor of the first component into the aqueous suspension;
(3) heating the mixture obtained in step (2) until the solvent evaporates to obtain a paste;
(4) drying and calcining the paste obtained in step (3);
(5) mixing the powder obtained in step (4), a sol comprising cerium and zirconium and nitric acid, and grinding the mixture to obtain a slurry;
(6) impregnating a porous support with the slurry obtained in step (5); and
(7) drying and calcining the object treated in step (6).

24. Use of a catalyst according to any one of Claims 1-12, characterized in that it is for the selective reduction of a nitrogen oxide emitted by a stationary or a mobile source.

25. Use of a catalyst according to Claim 24, characterized in that it is for the selective reduction of a nitrogen oxide emitted by an internal combustion engine.

26. Use of a catalyst according to claim 24 or claim 25, characterized in that ammonia or urea is used as a reducing agent.
FIG. 5A

FIG. 5B

FIG. 6
FIG. 11

FIG. 12
FIG. 19