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DESCRIPTION

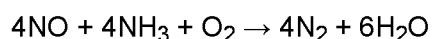
FIELD OF THE INVENTION

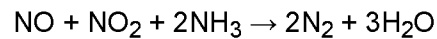
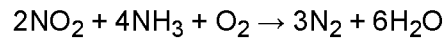
[0001] The present invention is directed towards catalysts and methods for removal of ammonia from flue gases that have been subjected to selective catalytic reduction (SCR) of oxides of nitrogen (NO_x) by ammonia injection. More specifically, the present invention is directed to a composite catalyst having a layer comprising an SCR catalyst and a layer comprising an oxidation catalyst, where the oxidation catalyst comprises at least two metals chosen from specific groups, and the layer comprising the oxidation catalyst does not contain a platinum group metal (PGM).

BACKGROUND OF THE INVENTION

[0002] Combustion of hydrocarbon-based fuel in electrical power stations and in engines produces flue or exhaust gas that contains, in large part, relatively benign nitrogen (N₂), water vapor (H₂O), and carbon dioxide (CO₂). But the flue and exhaust gases also contains, in relatively small part, noxious and/or toxic substances, such as carbon monoxide (CO) from incomplete combustion, hydrocarbons (HC) from un-burnt fuel, nitrogen oxides (NO_x) from excessive combustion temperatures, and particulate matter (mostly soot). To mitigate the environmental impact of flue and exhaust gas released into the atmosphere, it is desirable to eliminate or reduce the amount of the undesirable components, preferably by a process that, in turn, does not generate other noxious or toxic substances.

[0003] Typically, flue gases from electrical power stations and exhaust gases lean burn gas engines have a net oxidizing effect due to the high proportion of oxygen that is provided to ensure adequate combustion of the hydrocarbon fuel. In such gases, one of the most burdensome components to remove is NO_x, which includes nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O). The reduction of NO_x to N₂ is particularly problematic because the exhaust gas contains enough oxygen to favor oxidative reactions instead of reduction. Notwithstanding, NO_x can be reduced by a process commonly known as Selective Catalytic Reduction (SCR). An SCR process involves the conversion of NO_x, in the presence of a catalyst and with the aid of a nitrogenous reducing agent, such as ammonia, into elemental nitrogen (N₂) and water. In an SCR process, a gaseous reductant such as ammonia is added to an exhaust gas stream prior to contacting the exhaust gas with the SCR catalyst. The reductant is absorbed onto the catalyst and the NO_x reduction reaction takes place as the gases pass through or over the catalyzed substrate. The chemical equation for stoichiometric SCR reactions using ammonia is:





[0004] Most SCR processes utilize a stoichiometric excess of ammonia in order to maximize the conversion of NO_x. Unreacted ammonia that passes through the SCR process (also referred to as "ammonia slip") is undesirable, because the released ammonia gas can negatively impact the atmosphere and can react with other combustion species. To reduce ammonia slip, SCR systems can include an ammonia oxidation catalyst (AMOX) (also known as an ammonia slip catalyst (ASC)) downstream of the SCR catalyst.

[0005] Catalysts for oxidizing excess ammonia in an exhaust gas are known. For example, US Pat. No. 7,393,511 describes an ammonia oxidation catalyst containing a precious metal, such as platinum, palladium, rhodium, or gold on a support of titania alumina, silica, zirconia, etc. Other ammonia oxidation catalyst contain a first layer of vanadium oxide, tungsten oxide, and molybdenum oxide on a titania support, and a second layer of platinum on a titania support (see, e.g., US Pat. Nos. 8,202,481 and US 7,410,626). However, these catalysts are not highly efficient at converting ammonia, particularly at relatively low temperatures. Most of the known systems for oxidizing excess ammonia rely of expensive precious metals as a component in the oxidation catalyst. Accordingly, there remains a need in the art for improved ammonia slip catalysts. The present invention satisfies this need among others. US2008/112870 relates to oxidation catalysts and oxidation catalyst systems for oxidizing both ammonia and carbon monoxide.

[0006] US2010/111796 relates to catalysts and method for preparing catalysts and methods for treating emissions in exhaust gas.

[0007] WO2012/160391 relates to an exhaust gas oxidation catalyst for the clean-up of exhaust gas discharged from internal combustion engines.

[0008] US2009/209408 relates to an exhaust-gas purifying catalyst, particularly to an exhaust gas-purifying catalyst including oxygen storage material.

[0009] US2012/042631 relates to exhaust after-treatment systems that treat the exhaust produced by a lean-burn engine and, more particularly, to catalyst materials that may be used to oxidize ammonia, among others, and help prevent ammonia slip to the atmosphere.

SUMMARY OF THE INVENTION

[0010] In an aspect, the invention provides a dual layer ammonia slip catalyst can comprise a layer comprising an SCR catalyst layer, an oxidation catalyst layer and a substrate, wherein the SCR catalyst layer comprises a molecular sieve or a vanadium/titania SCR catalyst and the oxidation catalyst layer comprises an oxidation catalyst, where the oxidation catalyst comprises at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and a second metal which is manganese (Mn), where the ammonia slip catalyst does not comprise a platinum group metal and wherein at least the oxidation layer is positioned proximal to the substrate. The layer comprising the SCR catalyst is also called the SCR layer, and the layer comprising the oxidation catalyst is also called the oxidation layer.

[0011] Described herein but falling outside the scope of the claims is a method for producing an ammonia slip catalyst comprises: (a) forming a washcoat comprising a mixture of the SCR catalyst and an oxidation catalyst comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), and the ammonia slip catalyst does not comprise a platinum group metal; (b) applying the washcoat to a substrate; (c) drying the washcoat on the substrate; and (d) calcining the washcoat on the substrate.

[0012] Described herein but falling outside the scope of the claims is a method for producing a dual layer ammonia slip catalyst comprises: (a) forming an oxidation layer on a substrate by applying onto a substrate a oxidation layer washcoat comprising an oxidation catalyst comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), where the ammonia slip catalyst does not comprise a platinum group metal, (b) drying the oxidation layer washcoat on the substrate, (c) calcining the oxidation layer washcoat on the substrate, (d) forming an SCR layer positioned over the oxidation layer by applying an SCR layer washcoat comprising an SCR catalyst over the calcined oxidation layer on a substrate formed in step (c), (e) drying the SCR layer washcoat on the calcined oxidation layer on a substrate and (f) calcining the SCR layer washcoat on the calcined oxidation layer washcoat on the substrate.

[0013] Described herein but falling outside the scope of the claims is a method for producing a dual layer ammonia slip catalyst comprises (a) forming an oxidation layer on a substrate by placing on the substrate an oxidation layer washcoat comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum

(Mo), tin (Sn), tantalum (Ta), and strontium (Sr), and the ammonia slip catalyst does not comprise a platinum group metal, (b) drying the oxidation layer washcoat on the substrate, (c) forming an SCR layer positioned over the oxidation layer by applying an SCR washcoat comprising an SCR catalyst over the oxidation layer on a substrate formed in step (b), (d) drying the SCR layer washcoat on the calcined oxidation layer on the substrate and (e) calcining the oxidation layer washcoat and the SCR layer washcoat on the substrate.

[0014] Described herein but falling outside the scope of the claims is a method for producing a dual layer ammonia slip catalyst comprises (a) forming an SCR layer of an SCR catalyst on a substrate by applying onto a portion of a substrate a washcoat comprising an SCR catalyst; (b) drying the SCR washcoat layer on the substrate; (c) optionally calcining the SCR washcoat layer on the substrate; (d) forming an oxidation layer of an oxidation catalyst comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), and the ammonia slip catalyst does not comprise a platinum group metal, onto a portion of the substrate by applying onto a portion of a substrate a oxidation washcoat comprising the oxidation catalyst; (e) drying the oxidation layer on the substrate; and (f) calcining at least the oxidation catalyst on the substrate.

[0015] Also described herein but falling outside the scope of the claims are methods for reducing the concentration of ammonia in a flue gas stream generated by a combustion source comprise contacting a flue gas stream containing ammonia with the ammonia slip catalyst or a dual layer ammonia slip catalyst as described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The invention may be understood from the following detailed description when read in connection with the accompanying drawing.

Figures 1A-1L are drawings of configurations of catalyst articles showing locations of the SCR catalyst and the oxidations catalyst. Figures 1B-1F, 1I, 1J are in accordance with the claimed invention. Figures 1A, 1G, 1H, 1K and 1L are not in accordance with the claimed invention.

Figure 2 is a graph illustrating the percentage of NH₃ conversion in the ammonia slip catalyst zone according to an embodiment of a catalyst of the present invention as compared NH₃ conversions using two different platinum group metal based catalysts.

Figure 3 is a graph illustrating the percentage of NO_x selectivity in the ammonia slip catalyst zone according to an embodiment of a catalyst of the present invention as compared NH₃ conversions using two different platinum group metal based catalysts.

Figure 4 is a graph illustrating the total NH₃ and NO_x output (in ppm) in the ammonia slip catalyst zone according to an embodiment of a catalyst of the present invention as compared NH₃ conversions using two different platinum group metal based catalysts.

DETAILED DESCRIPTION OF THE INVENTION

[0017] As used in this specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly indicates otherwise. Thus, for example, reference to "a catalyst" includes a mixture of two or more catalysts, and the like.

[0018] As used herein, the term "calcine", or "calcination", means heating the material in air or oxygen. This definition is consistent with the IUPAC definition of calcination. (IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook.) Calcination is performed to decompose a metal salt and promote the exchange of metal ions within the catalyst and also to adhere the catalyst to a substrate. The temperatures used in calcination depend upon the components in the material to be calcined and generally are between about 400 °C to about 900 °C for approximately 1 to 8 hours. In some cases, calcination can be performed up to a temperature of about 1200 °C. In applications involving the processes described herein, calcinations are generally performed at temperatures from about 400 °C to about 700 °C for approximately 1 to 8 hours, preferably at temperatures from about 400 °C to about 650 °C for approximately 1 to 4 hours.

[0019] As used herein, the term "about" means approximately and refers to a range that is optionally $\pm 25\%$, preferably $\pm 10\%$, more preferably, $\pm 5\%$, or most preferably $\pm 1\%$ of the value with which the term is associated.

[0020] When a range, or ranges, for various numerical elements are provided, the range, or ranges, can include the values, unless otherwise specified.

[0021] The term "platinum group metal" or PGM, means ruthenium, rhodium, palladium, osmium, iridium, and platinum. The phrase "does not comprise a platinum group metal" means that a platinum group metal is not added in forming the catalyst but does not preclude one or more platinum group metals being present in trace amounts, which are levels that do not have measureable catalytic activity.

[0022] In an arrangement described herein that falls outside the scope of the claims, an ammonia slip catalyst comprises a mixture of an SCR catalyst and an oxidation catalyst, where the oxidation catalyst comprises at least one first metal selected from the group consisting of

copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), and the ammonia slip catalyst does not comprise a platinum group metal.

[0023] The invention provides a dual layer ammonia slip catalyst comprises an SCR layer comprising an SCR catalyst layer, an oxidation catalyst layer and a substrate, wherein the SCR catalyst layer comprises an SCR catalyst comprising a molecular sieve or a vanadium/titania SCR catalyst and the oxidation layer comprises an oxidation catalyst comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and a second metal, which is manganese (Mn), wherein the oxidation layer does not comprise a platinum group metal and wherein at least the oxidation catalyst layer is positioned proximal to the substrate. The layer comprising the SCR catalyst is also called the SCR layer, and the layer comprising the oxidation catalyst is also called the oxidation layer.

SCR CATALYST

[0024] The SCR catalyst can be an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof. The base metal can be selected from the group consisting of vanadium (V), molybdenum (Mo) and tungsten (W), chromium (Cr), cerium (Ce), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), and copper (Cu), and mixtures thereof. SCR compositions consisting of vanadium supported on a refractory metal oxide such as alumina, silica, zirconia, titania, ceria and combinations thereof are well known and widely used commercially in mobile applications. Typical compositions are described in U.S. Pat. Nos. 4,010,238 and 4,085,193. Compositions used commercially, especially in mobile applications, comprise TiO_2 on to which WO_3 and V_2O_5 have been dispersed at concentrations ranging from 5 to 20 wt. % and 0.5 to 6 wt. %, respectively. These catalysts may contain other inorganic materials such as SiO_2 and ZrO_2 acting as binders and promoters.

[0025] When the SCR catalyst is a base metal, the catalyst article can further comprise at least one base metal promoter. As used herein, a "promoter" is understood to mean a substance that when added into a catalyst, increases the activity of the catalyst. The base metal promoter can be in the form of a metal, an oxide of the metal, or a mixture thereof. The at least one base metal catalyst promoter may be selected from neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), strontium (Sr) and oxides thereof. The at least one base metal catalyst promoter can preferably be MnO_2 , Mn_2O_3 , Fe_2O_3 , SnO_2 , CuO , CoO , CeO_2 and mixtures thereof. The at least one base metal catalyst promoter may be added to the catalyst in the form of a salt in an aqueous solution, such as a nitrate or an acetate. The at least one base metal catalyst promoter and at least one base metal catalyst, e.g., copper, may be impregnated from an aqueous solution

onto the oxide support material(s), may be added into a washcoat comprising the oxide support material(s), or may be impregnated into a support previously coated with the washcoat. The SCR catalyst can contain from at least about 0.1 weight percent, at least about 0.5 weight percent, at least about 1 weight percent, or at least about 2 weight percent to at most about 10 weight percent, about 7 weight percent, about 5 weight percent of a promoter metal based on the total weight of the promoter metal and support.

[0026] The SCR catalyst can comprises a molecular sieve or a metal exchanged molecular sieve. As is used herein "molecular sieve" is understood to mean a metastable material containing tiny pores of a precise and uniform size that may be used as an adsorbent for gases or liquids. The molecules which are small enough to pass through the pores are adsorbed while the larger molecules are not. The molecular sieve can be a zeolitic molecular sieve, a non-zeolitic molecular sieve, or a mixture thereof.

[0027] A zeolitic molecular sieve is a microporous aluminosilicate having any one of the framework structures listed in the Database of Zeolite Structures published by the International Zeolite Association (IZA). The framework structures include, but are not limited to those of the CHA, FAU, BEA, MFI, MOR types. Non-limiting examples of zeolites having these structures include chabazite, faujasite, zeolite Y, ultrastable zeolite Y, beta zeolite, mordenite, silicalite, zeolite X, and ZSM-5. Aluminosilicate zeolites can have a silica/alumina molar ratio (SAR) defined as $\text{SiO}_2/\text{Al}_2\text{O}_3$ from at least about 5, preferably at least about 20, with useful ranges of from about 10 to 200.

[0028] As used herein, the term "non zeolitic molecular sieve" refers to corner sharing tetrahedral frameworks where at least a portion of the tetrahedral sites are occupied by an element other than silicon or aluminum. Specific non-limiting examples of non-zeolitic molecular sieves include silicoaluminophosphates such as SAPO-34, SAPO-37 and SAPO-44. The silicoaluminophosphates can have framework structures that contain framework elements that are found in zeolites, such as CHA, FAU, BEA, MFI, MOR and other types described below.

[0029] The SCR catalyst can comprise a small pore, a medium pore or a large pore molecular sieve, or combinations thereof.

[0030] The SCR catalyst can comprise a small pore molecular sieve selected from the group consisting of aluminosilicate molecular sieves, metal-substituted aluminosilicate molecular sieves, aluminophosphate (AIPO) molecular sieves, metal-substituted aluminophosphate (MeAIPO) molecular sieves, silico-aluminophosphate (SAPO) molecular sieves, and metal substituted silico-aluminophosphate (MeAPSO) molecular sieves, and mixtures thereof. The SCR catalyst can comprise a small pore molecular sieve selected from the group of Framework Types consisting of ACO, AEI, AEN, AFN, AFT, AFX, ANA, APC, APD, ATT, CDO, CHA, DDR, DFT, EAB, EDI, EPI, ERI, GIS, GOO, IHW, ITE, ITW, LEV, KFI, MER, MON, NSI, OWE, PAU, PHI, RHO, RTH, SAT, SAV, SIV, THO, TSC, UEI, UFI, VNI, YUG, and ZON, and mixtures and/or intergrowths thereof. Preferably the small pore molecular sieve is selected

from the group of Framework Types consisting of CHA, LEV, AEI, AFX, ERI, SFW, KFI, DDR and ITE.

[0031] The SCR catalyst comprises can comprise a medium pore molecular sieve selected from the group of Framework Types consisting of AEL, AFO, AHT, BOF, BOZ, CGF, CGS, CHI, DAC, EUO, FER, HEU, IMF, ITH, ITR, JRY, JSR, JST, LAU, LOV, MEL, MFI, MFS, MRE, MTT, MVY, MWW, NAB, NAT, NES, OBW, -PAR, PCR, PON, PUN, RRO, RSN, SFF, SFG, STF, STI, STT, STW, -SVR, SZR, TER, TON, TUN, UOS, VSV, WEI, and WEN, and mixtures and/or intergrowths thereof. Preferably, the medium pore molecular sieve selected from the group of Framework Types consisting of MFI, FER and STT.

[0032] The SCR catalyst can comprise a large pore molecular sieve selected from the group of Framework Types consisting of AFI, AFR, AFS, AFY, ASV, ATO, ATS, BEA, BEC, BOG, BPH, BSV, CAN, CON, CZP, DFO, EMT, EON, EZT, FAU, GME, GON, IFR, ISV, ITG, IWR, IWS, IWW, IXX, JSR, LTF, LTL, MAZ, MEI, MOR, MOZ, MSE, MTW, NPO, OFF, OKO, OSI, -RON, RWY, SAF, SAO, SBE, SBS, SBT, SEW, SFE, SFO, SFS, SFV, SOF, SOS, STO, SSF, SSY, USI, UWY, and VET, and mixtures and/or intergrowths thereof. Preferably, the large pore molecular sieve is selected from the group of Framework Types consisting of MOR, OFF and BEA.

[0033] A metal exchanged molecular sieve can have at least one metal from one of the groups VB, VIB, VIIB, VIIIB, IB, or IIB of the periodic table deposited onto extra-framework sites on the external surface or within the channels, cavities, or cages of the molecular sieves. Metals may be in one of several forms, including, but not limited to, zerovalent metal atoms or clusters, isolated cations, mononuclear or polynuclear oxycations, or as extended metal oxides. Preferably, the metals can be iron, copper, and mixtures or combinations thereof.

[0034] The metal can be combined with the zeolite using a mixture or a solution of the metal precursor in a suitable solvent. The term "metal precursor" means any compound or complex that can be dispersed on the zeolite to give a catalytically-active metal component. Preferably the solvent is water due to both economics and environmental aspects of using other solvents. When copper, a preferred metal is used, suitable complexes or compounds include, but are not limited to, anhydrous and hydrated copper sulfate, copper nitrate, copper acetate, copper acetylacetonate, copper oxide, copper hydroxide, and salts of copper amines (e.g. $[\text{Cu}(\text{NH}_3)_4]^{2+}$). This invention is not restricted to metal precursors of a particular type composition, or purity. The molecular sieve can be added to the solution of the metal component to form a suspension, which is then allowed to react so that the metal component is distributed on the zeolite. The metal can be distributed in the pore channels as well as on the outer surface of the molecular sieve. The metal can be distributed in ionic form or as a metal oxide. For example, copper may be distributed as copper (II) ions, copper (I) ions, or as copper oxide. The molecular sieve containing the metal can be separated from the liquid phase of the suspension, washed, and dried. The resulting metal-containing molecular sieve can then be calcined to fix the metal in the molecular sieve.

[0035] A metal exchanged molecular sieve can contain in the range of about 0.10% and about

10% by weight of a group VB, VIB, VIIB, VIIIB, IB, or IIB metal located on extra framework sites on the external surface or within the channels, cavities, or cages of the molecular sieve. Preferably, the extra framework metal can be present in an amount of in the range of about 0.2% and about 5% by weight.

[0036] The metal exchanged molecular sieve can be a copper (Cu) supported small pore molecular sieve having from about 0.1 to about 20.0 wt. % copper of the total weight of the catalyst. Preferably copper is present from a about 1 wt. % to about 6 wt. % of the total weight of the catalyst, more preferably from about 1.8 wt. % to about 4.2 wt. % of the total weight of the catalyst.

[0037] The metal exchanged molecular sieve can be an iron (Fe) supported small pore molecular sieve having from about 0.1 to about 20.0 wt. % iron of the total weight of the catalyst. Preferably iron is present from about 1 wt. % to about 6 wt. % of the total weight of the catalyst, more preferably from about 1.8 wt. % to about 4.2 wt. % of the total weight of the catalyst.

OXIDATION CATALYST

[0038] The oxidation catalyst comprises at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and a second metal, which is manganese (Mn), wherein the ammonia slip catalyst does not comprise a platinum group metal.

[0039] Each of the at least one first metal and the second metal can be in the form of a salt, preferably a nitrate, sulfate, chloride or an acetate, an oxide, or a compound containing the metal where the compound containing the metal forms an oxide of the metal upon calcination. Preferably the first metal is Cu.

[0040] A layer comprising an oxidation catalyst can further comprise an oxide support material comprising alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), ceria (CeO_2) and titania (TiO_2), or mixtures thereof. The oxide support material can further comprise other oxide materials such as perovskites, nickel oxide (NiO), manganese dioxide (MnO_2), praseodymium (III) oxide (Pr_2O_3). The oxide support material can include composite oxides or mixed oxides of two or more thereof (such as CeZrO_2 mixed oxides, TiZrO_2 mixed oxides, TiSiO_2 mixed oxides, and TiAlO_x oxides where x is dependent on the ratio of TiO_2 to Al_2O_3 .) The oxide support material, in addition for serving as a support may also serve as a binder. For example, alumina may act as both a support and a binder in an alumina and CeZrO_2 mixed oxide. The second layer can comprise an oxide support material comprising one or more of a stabilized alumina, silica, zirconia, ceria, and titania. Stabilizers may be selected from zirconium (Zr), lanthanum (La), aluminum (Al), yttrium (Y), praseodymium (Pr), neodymium (Nd), an oxide thereof, a composite oxide or mixed oxide of any two or more thereof, or at least one alkaline earth

metal, e.g., barium (Ba). If each oxide support material is stabilized, the stabilizers may be the same or different. The oxide support material can be Al_2O_3 and CeO_2 . Where the oxide support material is Al_2O_3 , it may be alpha-, gamma-, beta-, delta-, or theta- Al_2O_3 , for example. The support material can be in the form of mixed oxides or stabilized mixed oxides. The metal oxides in mixed oxides are present in the form of a single phase, while stabilized mixed oxides are present in two phases. Preferably a layer comprising the oxidation catalyst comprises Cu and Mn, as the first and second metals, alumina and either $\text{CeO}_2/\text{ZrO}_2$ or a Zr-stabilized CeO_2 mixed oxide. The Zr-stabilized CeO_2 mixed oxide can comprise Ce and Zr in about a 1:1 mole ratio. The oxide support material can be La-stabilized Al_2O_3 and Zr-stabilized CeO_2 . The oxide support material in the second layer can comprise about 20 mole % La-stabilized Al_2O_3 and about 80 mole % Zr-stabilized CeO_2 .

SUBSTRATE

[0041] The term "substrate" refers to substantially inert substrate material, as generally known in the art. The substrate may be of any generally suitable form. For example, the substrate may comprise a flow through monolith, such as a ceramic or honeycomb structure, or the substrate may be in the form of foams, or the substrate may be in the form of pellets, fluidized bed particulates, or may comprise particles such as spheres or short extruded segments.

[0042] The solid substrate may be any of those materials typically used for preparing exhaust gas treatment catalysts and will preferably comprise a metal or refractory ceramic having a honeycomb structure. Any suitable substrate may be employed, such as a monolithic substrate of the type having a plurality of fine, parallel gas flow passages extending there through from an inlet or an outlet face of the carrier, such that passages are open to fluid flow there through. The passages that are essentially straight paths from their fluid inlet to their fluid outlet are defined by walls on which the ammonia oxidation catalyst is coated as a "washcoat" so that the gases flowing through the passages contact the catalytic material. The flow passages of the monolithic carrier are thin-walled channels which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, circular, etc. Such structures may contain from about 60 to about 600 or more gas inlet openings (i.e., "cells") per square inch of cross section.

[0043] Honeycomb substrates comprise multiple adjacent, parallel channels that generally extend from the inlet face to the outlet face of the substrate and are either open on both ends (flow-through substrates) or are capped on alternating ends in a checker-board type pattern (wall-flow filters). This geometry results in a high-surface area-to-volume ratio. Honeycomb configurations are more compact than plate types, but have higher pressure drops and plug more easily. However, for most mobile applications, preferred substrates are honeycombs. For certain applications, the honeycomb flow through monolith has a high cell density, for example about 93-124 cells/cm² (600 to 800 cells per square inch), and/or an average internal wall

thickness of about 0.18 - 0.35 mm, preferably about 0.20 - 0.25 mm. For certain other applications, the honeycomb flow through monolith preferably has a low cell density of about 23.3 - 93.0 cells/cm² (150 - 600 cells per square inch), more preferably about 31-62 cells/cm² (200 - 400 cells per square inch). Preferably, the honeycomb monoliths are porous. In addition to cordierite, silicon carbide, silicon nitride, ceramic, and metal, other materials that can be used for the substrate include aluminum nitride, silicon nitride, aluminum titanate, α -alumina, mullite e.g. acicular mullite, pollucite, a thermet such as Al₂O₃ZFe, Al₂O₃/Ni or B₄CZFe, or composites comprising segments of any two or more thereof. Preferred materials include cordierite, silicon carbide, and alumina titanate. In certain embodiments, the substrate is inert.

[0044] The substrate wall of a honeycomb preferably has a porosity and pore size that is conducive for washcoating. Porosity is a measure of the percentage of void space in a porous substrate. Preferably, the porous substrate has a porosity of about 30 to about 80%, for example about 40 to about 75%, about 40 to about 65%, or from about 50 to about 60%. The pore interconnectivity, measured as a percentage of the substrate's total void volume, is the degree to which pores, void, and/or channels, are joined to form continuous paths through a porous substrate, i.e., from the inlet face to the outlet face of a filter. Preferably, the porous substrate has a pore interconnectivity volume of at least about 30%, more preferably at least about 40%.

[0045] Mean pore size of the substrate wall can be determined by any acceptable means, including by mercury porosimetry. Preferred porous substrates have a mean pore size of about 10 to about 40 μ m, for example about 20 to about 30 μ m, about 10 to about 25 μ m, about 10 to about 20 μ m, about 20 to about 25 μ m, about 10 to about 15 μ m, and about 15 to about 20 μ m.

WASHCOAT

[0046] The term "washcoat" is a term widely recognized in the art and refers to mixture of one or more a catalyst or a catalysts precursor, support materials, and optionally other materials such as binders, promoters or stabilizers.

[0047] The catalysts of the present invention can be utilized in heterogeneous catalytic reaction systems (i.e., solid catalyst in contact with a gas reactant). To improve contact surface area, mechanical stability, and fluid flow characteristics, the catalyst components can be disposed on and/or within a substrate, for example as a coating. In certain embodiments, a washcoat containing one or more of the catalyst components is applied as a coating to an inert substrate, such as corrugated metal plate or a honeycomb cordierite brick. The washcoat is preferably a solution, suspension, or slurry. Suitable coatings include surface coatings that cover a portion or the entire substrate, coatings that penetrate a portion of the substrate, coatings that permeate the substrate, or some combination thereof. In addition to the catalyst component, a washcoat can also include components, such as fillers, binders, stabilizers, rheology modifiers, and other additives, including one or more of alumina, silica, non-zeolite

silica alumina, titania, zirconia, ceria. In certain embodiments, the washcoat comprises pore-forming agents such as graphite, cellulose, starch, polyacrylate, and polyethylene, and the like. These additional components do not necessarily catalyze the desired reaction, but instead improve the catalytic material's effectiveness, for example by increasing its operating temperature range, increasing contact surface area of the catalyst, increasing adherence of the catalyst to a substrate, modifying rheology for better processing, etc. Typically, metal oxide particles used as binders are distinguishable over metal oxide particles used as supports based on particle size, with the binder particles being significantly larger relative to support particles.

[0048] A variety of deposition methods are known in the art for depositing the catalyst on the substrate. Methods for depositing the catalyst on the substrate include, for example, disposing the catalyst in a liquid vehicle to form a slurry and wetting the substrate with the slurry by dipping the substrate into the slurry, spraying the slurry onto the substrate, etc. A washcoat is typically applied to a substrate as a water-based slurry. Typically, the slurry will contain a total water content of at least 20 wt. %. Water contents of at least 30 wt. %, at least 40 wt. %, at least 50 wt. % or at least 60 wt. %, are also exemplified. The slurry coated substrate can be dried and calcined (thermally treated in presence of air or oxygen) prior to use. The temperatures and times used in calcination depend upon the components in the material to be calcined and generally are between about 400 °C to about 900 °C. In applications involving the processes described herein, calcinations are generally performed at temperatures from about 500 °C to about 550 °C for about 2 to about 6 hours.

[0049] The support for the oxidation catalyst can be kneaded along with other components such as fillers, binders, and reinforcing agents, into an extrudable paste which is then extruded through a die to form a honeycomb brick. Before or after the honeycomb brick is dried and/or calcined, the metal components of the oxidation catalyst are added to either one or more portions of the brick or to the entire brick in order to form the oxidation catalyst. In other embodiments, the oxidation catalyst containing the supported metals can be incorporated into the extrudable paste prior to extrusion. The SCR catalyst can then be applied as a coating on the extruded brick containing the oxidation catalyst. Two substrate designs useful in the present invention are plate and honeycomb. Plate-type catalysts have relative lower pressure drops and are less susceptible to plugging and fouling than the honeycomb types, but plate configurations are much larger and more expensive. The plates are typically constructed of metal or corrugated metal.

[0050] In certain embodiments, the washcoat or impregnation loading on and/or within the substrate for each layer or for the combination of two or more layers is 6.1 to 488.2 g/L (0.1 to 8 g/in³), more preferably 30.5 to 366.1 g/L (0.5 to 6 g/in³), and even more preferably 61 to 244 g/L (1 to 4 g/in³). In certain embodiments, the washcoat or impregnation loading on and/or within the substrate for each layer or for the combination of two or more layers is >61.02 g/L (1.00 g/in³), such as > 73.23 g/L (1.2 g/in³), > 91.54 g/L (1.5 g/in³), > 103.74 g/L (1.7 g/in³) or > 122.05 g/L (2.00 g/in³) or for example 91.5 to 152.6 g/L (1.5 to 2.5 g/in³).

CONFIGURATIONS OF SCR AND OXIDATION CATALYSTS

[0051] The SCR catalyst and the oxidation catalyst are configured such that there is an overlayer of an SCR catalyst on an underlayer of the oxidation catalyst that is placed on a substrate.

[0052] Figure 1A (not in accordance with the claimed invention) shows a configuration in which the SCR catalyst and the oxidation catalyst are present in a single layer 8 on the substrate 14.

[0053] Figure 1B shows a configuration in which the SCR layer 10 comprising the SCR catalyst is positioned over the oxidation layer 12 comprising the oxidation catalyst, and the oxidation layer 12 is positioned over the solid substrate. In Figure 1B, both the SCR layer and the oxidation layer are positioned over the entire axial length of the substrate. The SCR layer and the oxidation layer can be positioned over a portion of the axial length of the substrate, as shown in Figures 1C and 1D. In placing the SCR layer over the oxidation layer, a portion of the SCR washcoat can occupy some or all of the space between adjacent oxidation layers. Figure 1E shows where all of the space between adjacent oxidation layers comprises an SCR catalyst. The space between adjacent oxidation layers can be completely filled with an SCR overlay that also fills the space between the oxidation layers, as shown in Figure 1F. Generally, a catalyst layer of the present invention permeates the substrate; penetrates a portion of the substrate, for example a majority portion; coats the surface of the substrate; or a combination thereof. Alternatively to being coated on a substrate wall, the oxidation catalyst can be incorporated into a high porosity substrate, for example as an interior coating that permeates the wall or can be incorporated into extrudable paste which forms the substrate. Figure 1G (not in accordance with the claimed invention) shows a configuration in which the SCR catalyst is present in a layer over the substrate 14 and the oxidation catalyst is present in the substrate 14. One or more of the catalysts layers can cover only a portion of the substrate. For example a catalyst layer can be applied to about 10 percent of the length of the substrate, from the front of the substrate 46 or the rear of the substrate 48, relative to the overall direction of exhaust gas flow 50 through the substrate. The oxidation catalyst layer can be coated on a portion at the rear of the substrate 48. The catalyst layers can cover about 25 percent, about 50 percent, or about 75 percent of the substrate, preferably from the rear 48 or front 46 of the substrate. The catalyst coatings may be applied to the same or different portions of the substrate, but preferably the SCR catalyst layer completely covers the oxidation catalyst layer so that all exhaust gas being treated by the catalyst layers will first pass through the SCR layer before reaching the oxidation catalyst layer.

[0054] The SCR layer and the oxidation layer can be placed next to each other sequentially in the direction of exhaust gas flow. As used herein, the term "sequential" with respect to the layers means that each layer is contact with a substrate and that the layers as a whole are arranged next to one another on one or more substrates. Figure 1H (not in accordance with the claimed invention) shows a sequential positioning of an SCR layer 10 comprising an SCR

catalyst and an oxidation layer 12 comprising an oxidation catalyst on a solid support 14. The exhaust gas has a generalized flow in the direction of the arrow, from left to right. The support has a front end 46 and a back end 48.

[0055] Figure 1I shows a sequential positioning of an SCR layer 10 comprising an SCR catalyst and an oxidation layer 12 comprising an oxidation catalyst on a solid support 14. Part of the SCR layer 10 also is an overlayer over the oxidation layer 12. The overlayer can be located over the entire oxidation layer, as shown in Figure 1I, or over a portion of the oxidation layer, as shown in Figure 1J.

[0056] In arrangements not in accordance with the claimed invention, the SCR layer and the oxidation layer may be present on two different supports. An SCR layer 10 comprising the SCR catalyst can be placed on a support 14 with an adjacent, downstream support 15 having an oxidation layer 12 comprising the oxidation catalyst on the support is shown in Figure 1K (not in accordance with the claimed invention). An SCR layer 10 comprising the SCR catalyst can be placed on a support 14 with an opposite support 15 having an oxidation layer 12 comprising the oxidation catalyst on the support, as shown in Figure 1L (not in accordance with the claimed invention).

[0057] Importantly, in the present invention, the SCR catalyst is disposed over the oxidation catalyst layer. The SCR layer preferably covers the entire oxidation catalyst layer to prevent untreated secondary NO_x formed via ammonia oxidation in the oxidation layer from exiting the system without contacting the SCR catalyst.

[0058] Described herein but falling outside the scope of the claims is a method of manufacturing an ammonia slip catalyst comprising: (a) forming an layer on a substrate by applying onto the substrate a washcoat comprising an SCR catalyst and an oxidation catalyst comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), where the washcoat does not comprise a platinum group metal, (b) drying the washcoat on the substrate, and (c) calcining the washcoat on the substrate. Each of the at least one first metal and second metal can may be present in the oxidation layer washcoat in the form of a salt, preferably a nitrate, sulfate, chloride or an acetate, an oxide, or a compound containing the metal where the compound containing the metal forms an oxide of the metal upon calcination. Preferably the first metal is Cu and the second metal is Mn. The washcoat can further comprise an oxide support material comprising alumina (Al₂O₃), silica (SiO₂), zirconia (ZrO₂), ceria (CeO₂), and titania (TiO₂), or mixtures thereof. The washcoat can further comprise other oxide materials such as perovskites, nickel oxide (NiO), manganese dioxide (MnO₂), praseodymium (III) oxide (Pr₂O₃). The oxide support material can include composite oxides or mixed oxides of two or more thereof (such as CeZrO₂ mixed oxides, TiZrO₂ mixed oxides, TiSiO₂ mixed oxides, and

TiAlO_x oxides where x is dependent on the ratio of TiO₂ to Al₂O₃.) The oxide support material, in addition for serving as a support, may also serve as a binder. For example, alumina may act as both a support and a binder in an alumina and CeZrO₂ mixed oxide. The oxidation layer washcoat can comprise an oxide support material comprising one or more of a stabilized alumina, silica, zirconia, ceria, and titania. Stabilizers may be selected from zirconium (Zr), lanthanum (La), aluminum (Al), yttrium (Y), praseodymium (Pr), neodymium (Nd), an oxide thereof, a composite oxide or mixed oxide of any two or more thereof, or at least one alkaline earth metal, e.g., barium (Ba). If each oxide support material is stabilized, the stabilizers may be the same or different. The oxide support material can be Al₂O₃ and CeO₂. Where the oxide support material is Al₂O₃, it may be alpha-, gamma-, beta-, delta-, or theta-Al₂O₃, for example. The support material can be in the form of mixed oxides or stabilized mixed oxides. The metal oxides in mixed oxides are present in the form of a single phase, while stabilized mixed oxides are present in two phases. Preferably the washcoat comprises Cu and Mn, as the first and second metals, alumina and either CeO₂/ZrO₂ or a Zr-stabilized CeO₂ mixed oxide. The Zr-stabilized CeO₂ mixed oxide can comprise Ce and Zr in about a 1:1 mole ratio. The oxide support material can be La-stabilized Al₂O₃ and Zr-stabilized CeO₂. The oxide support material in the oxidation washcoat can comprise about 20 mole % La-stabilized Al₂O₃ and about 80 mole % Zr-stabilized CeO₂. The washcoat can comprise a molecular sieve selected from the group consisting of MOR (mordenite), FER (ferrierite), FAU (zeolite Y), MFI (ZSM-5), BEA (beta zeolites), Fe-BEA, CHA (Chabazite), Cu-CHA and a silicoaluminophosphate comprising a structurally similar framework. The washcoat can preferably comprise a Fe-BEA or a Cu-CHA zeolite catalyst or a silicoaluminophosphate comprising a structurally similar framework. Preferably, the washcoat can comprise a Fe-BEA or a Cu-CHA zeolite catalyst or a silicoaluminophosphate comprising a structurally similar framework and further comprises Cu and Mn. The oxidation catalyst in the washcoat can be present at a concentration of 0.02 to 0.09 g per cm³ (0.3 to 1.5 g per in³), based on the total weight of metal in the catalyst. The SCR catalyst in the washcoat can be present at a concentration of 0.03 to 0.15 g per cm³ (0.5 to 2.5 g per in³), based on the total weight of metal in the catalyst. The ratio of the amount of SCR catalyst in the washcoat (in g per cm³) to the amount of oxidation catalyst in the washcoat (in g per cm³) can be between 0.02 and 0.5. (The ratio of the amount of SCR catalyst in the washcoat (in g per in³) to the amount of oxidation catalyst in the washcoat (in g per in³) can be between 0.3 and 8.3.)

[0059] Described herein but falling outside the scope of the claims is a method of manufacturing a dual layer ammonia slip catalyst comprising : (a) forming an oxidation layer on a substrate by applying onto a substrate an oxidation layer washcoat comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), where the washcoat does not comprise a

platinum group metal, (b) drying the oxidation layer washcoat on the substrate, (c) calcining the oxidation layer washcoat on the substrate; (d) forming an SCR layer positioned over the oxidation layer by applying an SCR layer washcoat comprising a molecular sieve, preferably having a substituted metal and/or an extra framework metal, or a vanadium/titania over the calcined oxidation layer formed in step (c), (e) drying the SCR layer washcoat on the calcined oxidation layer on a substrate, and (f) calcining the SCR layer washcoat on the oxidation layer washcoat on the substrate. Each of the at least one first metal and second metal can be present in the oxidation layer washcoat in the form of a salt, preferably a nitrate, sulfate, chloride or an acetate, an oxide, or a compound containing the metal where the compound containing the metal forms an oxide of the metal upon calcination. Preferably the first metal is Cu and the second metal is Mn. The oxidation layer washcoat can further comprise an oxide support material comprising alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), ceria (CeO_2), and titania (TiO_2), or mixtures thereof. The oxide support material can further comprise other oxide materials such as perovskites, nickel oxide (NiO), manganese dioxide (MnO_2), praseodymium (III) oxide (Pr_2O_3). The oxide support material can include composite oxides or mixed oxides of two or more thereof (such as CeZrO_2 mixed oxides, TiZrO_2 mixed oxides, TiSiO_2 mixed oxides, and TiAlO_x oxides where x is dependent on the ratio of TiO_2 to Al_2O_3). The oxide support material, in addition for serving as a support may also serve as a binder. For example, alumina may act as both a support and a binder in an alumina and CeZrO_2 mixed oxide. The oxidation layer washcoat can comprise an oxide support material comprising one or more of a stabilized alumina, silica, zirconia, ceria, and titania. Stabilizers may be selected from zirconium (Zr), lanthanum (La), aluminum (Al), yttrium (Y), praseodymium (Pr), neodymium (Nd), an oxide thereof, a composite oxide or mixed oxide of any two or more thereof, or at least one alkaline earth metal, e.g., barium (Ba). If each oxide support material is stabilized, the stabilizers may be the same or different. The oxide support material can be Al_2O_3 and CeO_2 . Where the oxide support material is Al_2O_3 , it may be alpha-, gamma-, beta-, delta-, or theta- Al_2O_3 , for example. The support material can be in the form of mixed oxides or stabilized mixed oxides. The metal oxides in mixed oxides are present in the form of a single phase, while stabilized mixed oxides are present in two phases. Preferably the oxidation layer washcoat comprises Cu and Mn, as the first and second metals, alumina and either $\text{CeO}_2/\text{ZrO}_2$ or a Zr-stabilized CeO_2 mixed oxide. The Zr-stabilized CeO_2 mixed oxide can comprise Ce and Zr in about a 1:1 mole ratio. The oxide support material can be La-stabilized Al_2O_3 and Zr-stabilized CeO_2 . The oxide support material in the oxidation washcoat can comprise about 20 mole % La-stabilized Al_2O_3 and about 80 mole % Zr-stabilized CeO_2 . The SCR layer washcoat can comprise a molecular sieve selected from the group consisting of MOR (mordenite), FER (ferrierite), FAU (zeolite Y), MFI (ZSM-5), BEA (beta zeolites), Fe-BEA, CHA (Chabazite), Cu-CHA and a silicoaluminophosphate comprising a structurally similar framework. The SCR layer washcoat can preferably comprise a Fe-BEA or a Cu-CHA zeolite catalyst or a silicoaluminophosphate comprising a structurally similar framework. Preferably, the SCR layer washcoat can comprise a Fe-BEA or a Cu-CHA zeolite catalyst and the oxidation layer washcoat can comprise Cu and Mn. The catalyst in the oxidation layer washcoat can be present at a concentration of 0.02 to 0.09 g/cm^3 (0.3 to 1.5 g per in^3), based on the total weight of metal in the catalyst. The catalyst

in the SCR layer washcoat can be present at a concentration of 0.03 to 0.15 g/cm³ (0.5 to 2.5 g per in³), based on the total weight of metal in the catalyst. The ratio of the amount of catalyst in the SCR layer washcoat (in g per cm³) to the amount of catalyst in the oxidation layer washcoat (in g per cm³) can be between 0.02 and 0.5, based on the total weight of metal in each layer of the catalyst. (The ratio of the amount of catalyst in the SCR layer washcoat (in g per in³) to the amount of catalyst in the oxidation layer washcoat (in g per in³) can be between 0.3 and 8.3, based on the total weight of metal in each layer of the catalyst.)

[0060] Described herein but falling outside the scope of the claims is a method of manufacturing a dual layer ammonia slip catalyst comprising: (a) forming an oxidation layer on a substrate by applying onto a substrate an oxidation layer washcoat comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), where the washcoat does not comprise a platinum group metal, (b) forming a dried oxidation layer washcoat on the substrate, (c) forming an SCR layer positioned over the oxidation layer by applying an SCR layer washcoat comprising a molecular sieve, preferably having a substituted metal and/or an extra framework metal, or a vanadium/titania over the dried oxidation layer formed in step (b), (d) drying the SCR layer washcoat on the calcined oxidation layer on a substrate, and (e) calcining the SCR layer washcoat on the calcined oxidation layer washcoat on the substrate. Each of the at least one first metal and second metal can may be present in the oxidation layer washcoat in the form of a salt, preferably a nitrate, sulfate, chloride or an acetate, an oxide, or a compound containing the metal where the compound containing the metal forms an oxide of the metal upon calcination. Preferably the first metal is Cu and the second metal is Mn. The oxidation layer washcoat can further comprise an oxide support material comprising alumina (Al₂O₃), silica (SiO₂), zirconia (ZrO₂), ceria (CeO₂), and titania (TiO₂), or mixtures thereof. The oxide support material can further comprise other oxide materials such as perovskites, nickel oxide (NiO), manganese dioxide (MnO₂), praseodymium (III) oxide (Pr₂O₃). The oxide support material can include composite oxides or mixed oxides of two or more thereof (such as CeZrO₂ mixed oxides, TiZrO₂ mixed oxides, TiSiO₂ mixed oxides, and TiAlO_x oxides where x is dependent on the ratio of TiO₂ to Al₂O₃). The oxide support material, in addition for serving as a support may also serve as a binder. For example, alumina may act as both a support and a binder in an alumina and CeZrO₂ mixed oxide. The oxidation layer washcoat can comprise an oxide support material comprising one or more of a stabilized alumina, silica, zirconia, ceria, and titania. Stabilizers may be selected from zirconium (Zr), lanthanum (La), aluminum (Al), yttrium (Y), praseodymium (Pr), neodymium (Nd), an oxide thereof, a composite oxide or mixed oxide of any two or more thereof, or at least one alkaline earth metal, e.g., barium (Ba). If each oxide support material is stabilized, the stabilizers may be the same or different. The oxide support material can be Al₂O₃ and CeO₂. Where the oxide support material is Al₂O₃, it may be alpha-, gamma-, beta-, delta-, or theta-Al₂O₃, for example. The support material can

be in the form of mixed oxides or stabilized mixed oxides. The metal oxides in mixed oxides are present in the form of a single phase, while stabilized mixed oxides are present in two phases. Preferably the oxidation layer washcoat comprises Cu and Mn, as the first and second metals, alumina and either CeO₂/ZrO or a Zr-stabilized CeO₂ mixed oxide. The Zr-stabilized CeO₂ mixed oxide can comprise Ce and Zr in about a 1:1 mole ratio. The oxide support material can be La-stabilized Al₂O₃ and Zr-stabilized CeO₂. The oxide support material in the oxidation layer washcoat can comprise about 20 mole % La-stabilized Al₂O₃ and about 80 mole % Zr-stabilized CeO₂. The SCR layer washcoat can comprise a molecular sieve selected from the group consisting of MOR (mordenite), FER (ferrierite), FAU (zeolite Y), MFI (ZSM-5), BEA (beta zeolites), Fe-BEA, CHA (Chabazite), Cu-CHA and a silicoaluminophosphate comprising a structurally similar framework. The SCR layer washcoat can preferably comprise a Fe-BEA or a Cu-CHA zeolite catalyst. Preferably, the SCR layer washcoat can comprise a Fe-BEA or a Cu-CHA zeolite catalyst and the oxidation layer washcoat can comprise Cu and Mn. The catalyst in the oxidation layer washcoat can be present at a concentration of 0.02 to 0.09 g per cm³ (0.3 to 1.5 g per in³), based on the total weight of metal in the catalyst. The catalyst in the SCR layer washcoat can be present at a concentration of 0.03 to 0.15 g per cm³ (0.5 to 2.5 g per in³), based on the total weight of metal in the catalyst. The ratio of the amount of catalyst in the SCR layer washcoat (in g per cm³) to the amount of catalyst in the oxidation layer washcoat (in g per cm³) can be between 0.02 and 0.5, based on the total weight of metal in each layer of the catalyst. (The ratio of the amount of catalyst in the SCR layer washcoat (in g per in³) to the amount of catalyst in the oxidation layer washcoat (in g per in³) can be between 0.3 and 8.3, based on the total weight of metal in each layer of the catalyst.)

[0061] Described herein but falling outside the scope of the claims is a method for reducing the concentration of ammonia in a flue gas stream generated by a combustion source comprises contacting a flue gas stream comprising ammonia with either: (1) an ammonia slip catalyst comprising a mixture of an SCR catalyst, as described above, and an oxidation catalyst comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), and the ammonia slip catalyst does not comprise a platinum group metal; or (2) a dual layer ammonia slip catalyst comprising an SCR layer comprising a molecular sieve, preferably having a substituted metal and/or an extra framework metal, or a vanadium/titania and the oxidation layer comprising an oxidation catalyst comprising at least one first metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr) and at least one second metal selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr), and the second layer does not comprise a platinum group metal. Each of the at least one first metal and second metal can be in the form of a salt, preferably a nitrate, sulfate,

chloride or an acetate, an oxide, or a compound containing the metal where the compound containing the metal forms an oxide of the metal upon calcination. Preferably the first metal is Cu and the second metal is Mn. The second layer can further comprise an oxide support material comprising alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), ceria (CeO_2), and titania (TiO_2), or mixtures thereof. The oxide support material can further comprise other oxide materials such as perovskites, nickel oxide (NiO), manganese dioxide (MnO_2), praseodymium (III) oxide (Pr_2O_3). The oxide support material can include composite oxides or mixed oxides of two or more thereof (such as CeZrO_2 mixed oxides, TiZrO_2 mixed oxides, TiSiO_2 mixed oxides, and TiAlO_x oxides where x is dependent on the ratio of TiO_2 to Al_2O_3). The oxide support material, in addition for serving as a support may also serve as a binder. For example, alumina may act as both a support and a binder in an alumina and CeZrO_2 mixed oxide. The second layer can comprise an oxide support material comprising one or more of a stabilized alumina, silica, zirconia, ceria, and titania. Stabilizers may be selected from zirconium (Zr), lanthanum (La), aluminum (Al), yttrium (Y), praseodymium (Pr), neodymium (Nd), an oxide thereof, a composite oxide or mixed oxide of any two or more thereof, or at least one alkaline earth metal, e.g., barium (Ba). If each oxide support material is stabilized, the stabilizers may be the same or different. The oxide support material can be Al_2O_3 and CeO_2 . Where the oxide support material is Al_2O_3 , it may be alpha-, gamma-, beta-, delta-, or theta- Al_2O_3 , for example. The support material can be in the form of mixed oxides or stabilized mixed oxides. The metal oxides in mixed oxides are present in the form of a single phase, while stabilized mixed oxides are present in two phases. Preferably the second layer comprises Cu and Mn, as the first and second metals, alumina and either CeO_2/ZrO or a Zr-stabilized CeO_2 mixed oxide. The Zr-stabilized CeO_2 mixed oxide can comprise Ce and Zr in about a 1:1 mole ratio. The oxide support material can be La-stabilized Al_2O_3 and Zr-stabilized CeO_2 . The oxide support material in the second layer can comprise about 20 mole % La-stabilized Al_2O_3 and about 80 mole % Zr-stabilized CeO_2 . The first layer can comprise a zeolite selected from the group consisting of MOR (mordenite), FER (ferrierite), FAU (zeolite Y), MFI (ZSM-5), BEA (beta zeolites), Fe-BEA, CHA (Chabazite) and Cu-CHA, or a silicoaluminophosphate comprising a structurally similar framework. The first layer washcoat can preferably comprise a Fe-BEA or a Cu-CHA zeolite catalyst. Preferably, the first layer can comprise a Fe-BEA or a Cu-CHA zeolite catalyst and the second layer can comprise Cu and Mn. When the second layer comprises Cu and Mn, the conversion of NH_3 to N_2 can be more selective than when a PGM based second layer is used. The catalyst in the second layer can be present at a concentration of 0.02 to 0.09 g per cm^3 (0.3 to 1.5 g per in^3), based on the total weight of metal in the catalyst. The catalyst in the first layer can be present at a concentration of 0.03 to 0.15 g per cm^3 (0.5 to 2.5 g per in^3), based on the total weight of metal in the catalyst. The ratio of the amount of catalyst in the first layer (in g per cm^3) to the amount of catalyst in the second layer (in g per cm^3) can be between 0.02 and 0.5, based on the total weight of metal in each layer of the catalyst. (The ratio of the amount of catalyst in the first layer (in g per in^3) to the amount of catalyst in the second layer (in g per in^3) can be between 0.3 and 8.3, based on the total weight of metal in each layer of

the catalyst.)

[0062] The flue gas can contact the dual layer ammonia slip catalyst at temperatures from about 300° to about 500°C.

[0063] The use of the oxidation layer comprising the oxidation catalysts comprising at least one first metal and the at least one second metal from the groups of metal listed above eliminates the need for the use of platinum group metals (PGM) in the composition. This will significantly reduce the cost of the composite catalyst.

EXAMPLES

[0064] Although the invention is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope of the claims and without departing from the invention.

[0065] Three catalysts, each having a first layer and a second layer, were prepared. Each of the catalysts had an SCR layer comprising a Fe beta zeolite SCR catalyst. Example 1 contained Cu, Mn, CeO₂/ZrO₂, and alumina in an oxidation layer. Comparative Example 1 contained 0.18 g/L (5 g/ft³) Pt in an oxidation layer and Comparative Example 2 contained 0.71 g/L (20 g/ft³) Pd in an oxidation layer. In prior art, layered ammonia slip catalysts with a zeolite overlayer contained an underlayer with precious metals components here used to oxidize the incoming ammonia.

Example 1: Base Metal Ammonia Slip Catalyst (ASC)

[0066] The oxidation layer was prepared by mixing the required amount of unmilled CeO₂/ZrO₂ and deionized water to form a slurry. The CeO₂/ZrO₂ slurry was then milled to provide a d50 of 1.5-2.5µm. The milled CeO₂/ZrO₂ was mixed with a slurry of alumina slurry, then the required amount of manganese acetate crystals were added and the mixture was mixed for 4 hours. The required amount of copper nitrate was added and the slurry was mixed for 30 minutes. Actigum was then added slowly to thicken the slurry. The slurry was coated onto a 1484 cells/cm² (230 cpsi) cordierite substrate, dried then calcined at 500°C for about 3 hours. This resulted in a Cu loading of 13.2 g/L (375 g/ft³), a Mn loading of 21.1 g/L (600 g/ft³), an alumina loading of 0.03 g/cm³ (0.55 g/in³), and a CeO₂/ZrO₂ loading of 0.13 g/cm³ (2.2 g/in³).

[0067] The SCR layer was prepared by adding a BEA zeolite to a solution of iron nitrate and

mixing the slurry with a dispersion mixer. A slurry of milled alumina having a d_{50} of 3.4-4.2 μm and deionized water was added to the slurry containing the BEA zeolite and the resulting slurry was mixed. The required amount of binder, Disperal, was added to the slurry and the slurry was mixed before coating the oxidation layers.

[0068] The slurry was coated onto a 1484 cells/cm² (230 cpsi) cordierite substrate, dried then calcined at 500°C for about 3 hours. This resulted in an iron loading of 6.71 g/L (190 g/ft³), a BEA zeolite loading of 0.12 g/cm³ (1.90 g/in³) and an alumina loading of 0.01 g/cm³ (0.16 g/in³).

Comparative Example 1: Pt ASC

[0069] The first catalyst layer was prepared by mixing the required amount of an alumina washcoat having a d_{50} of about 3.4 - 4.2 μm and deionized water using a high shear mixer to form a slurry. Succinic acid was slowly added to the alumina slurry until the final concentration was about 3.5 g/L (100 g/ft³), and then the admixture was continuously stirred for at least 30 minutes. The required amount of platinum nitrate was added and the resulting admixture was stirred for an additional 60 minutes. Hydroxyethyl cellulose (Natrasol) was added and the slurry was mixed for 24 hours. The slurry was coated onto a 1484 cells/cm² (230 cpsi) cordierite substrate, dried then calcined at 500°C for about 3 hours. This resulted in a Pt loading of 0.31 g/cm³ (5 g/ft³) and an alumina loading of 0.02 g/cm³ (0.35g/in³).

[0070] The SCR layer was prepared and coated over the oxidation layers as described above in Example 1.

Comparative Example 2: Pd ASC

[0071] The first catalyst layer was prepared by mixing the required amount of an alumina washcoat having a d_{50} of about 3.4 - 4.2 μm and deionized water using a high shear mixer to form a slurry. Succinic acid was slowly added to the alumina slurry until the final concentration was about 3.5 g/L (100 g/ft³), and then the admixture was continuously stirred for at least 30 minutes. The required amount of palladium nitrate was added and the resulting admixture was stirred for an additional 60 minutes. Hydroxyethyl cellulose (Natrasol) was added and the slurry was mixed for 24 hours. The slurry was coated onto a 1484 cells/cm² (230 cpsi) cordierite substrate, dried then calcined at 500°C for about 3 hours. This resulted in a Pd loading of 0.7 g/L (20 g/ft³) and an alumina loading of 0.02 g/cm³ (0.35g/in³).

[0072] The SCR layer was prepared and coated over the oxidation layers as described above in Example 1.

[0073] Evaluation of the catalytic activity of the catalysts used a two zone system with an SCR catalyst in the front zone followed by different ammonia slip catalysts in the rear zone. The main constituents of the gas feed contained a mixture of 40 ppm NH₃ and 30ppm NO_x, with the remaining gas composition consisting of O₂, H₂O, CO₂, propane, propene, and N₂. The steady state testing was done between 250°C-500°C at a system GHSV of 20,000 (40,000 through each zone).

[0074] Fig. 2 shows that the catalyst of Example 1, a catalyst of the invention, was more effective than the catalyst of Comparative Example 2, which contained 0.7 g/L (20 g/ft³) Pd, in the conversion of NH₃ from 250 °C to 500 °C. The catalyst of Example 1 was especially more effective than the catalyst of Comparative Example 2 at temperatures from about 250 °C to about 350 °C. The catalyst of Example 1 was less effective in the conversion of NH₃ than the catalyst of Comparative Example 1, which contained 0.18 g/L (5 g/ft³) Pt, over this temperature range.

[0075] Fig. 3 shows that the catalyst of Example 1, a catalyst of the invention, was more effective than the catalyst of Comparative Example 2, which contained 0.7 g/L (20 g/ft³) Pd, in converting CO in the range from about 250 °C to about 300 °C. The catalyst of Example 1, a catalyst of the invention, was slightly less effective in converting CO than the catalysts of Comparative Examples 1 and 2 at temperatures from about 350 °C to about 500 °C.

[0076] Fig. 4 shows that the catalyst of Example 1, a catalyst of the invention, was more effective than the catalysts of Comparative Examples 1 and 2, which contained 0.18 g/L (5 g/ft³) Pt and 0.71 g/L (20 g/ft³) Pd, respectively, in lowering the total amounts of NH₃ and NO_x leaving the system at temperatures from about 300 °C to about 500 °C. At temperatures of about 400 °C to about 500 °C, the of Example 1 produced NH₃ and NO_x at levels that were about 60% to about 75% of those produced by Comparative Example 1, which contained 0.18 g/L (5 g/ft³) Pt.

REFERENCES CITED IN THE DESCRIPTION

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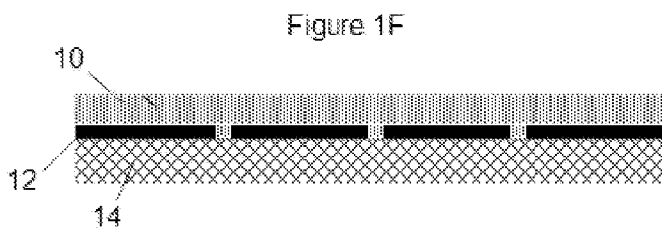
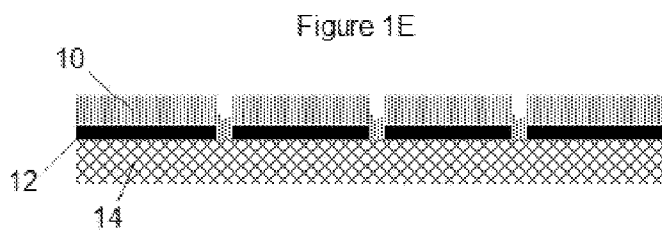
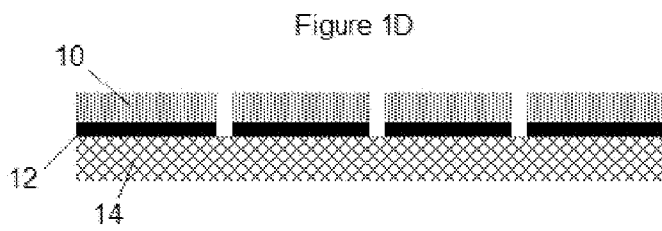
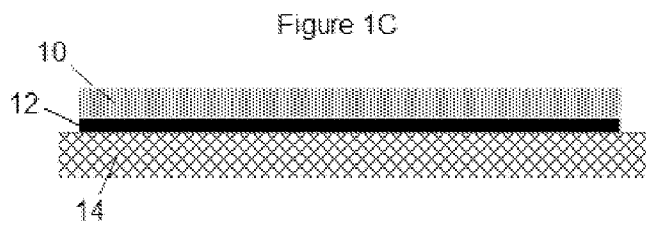
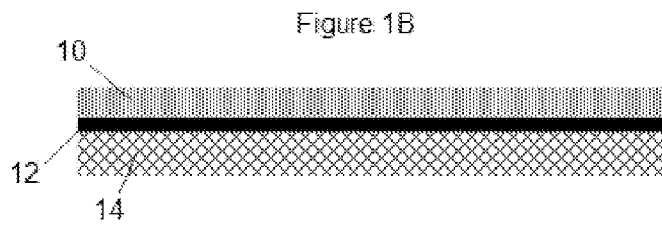
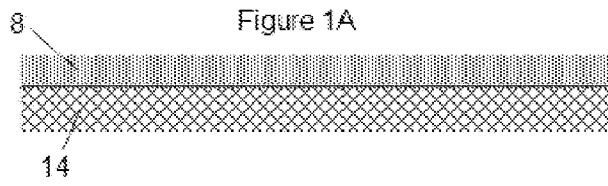
PATENTKRAV

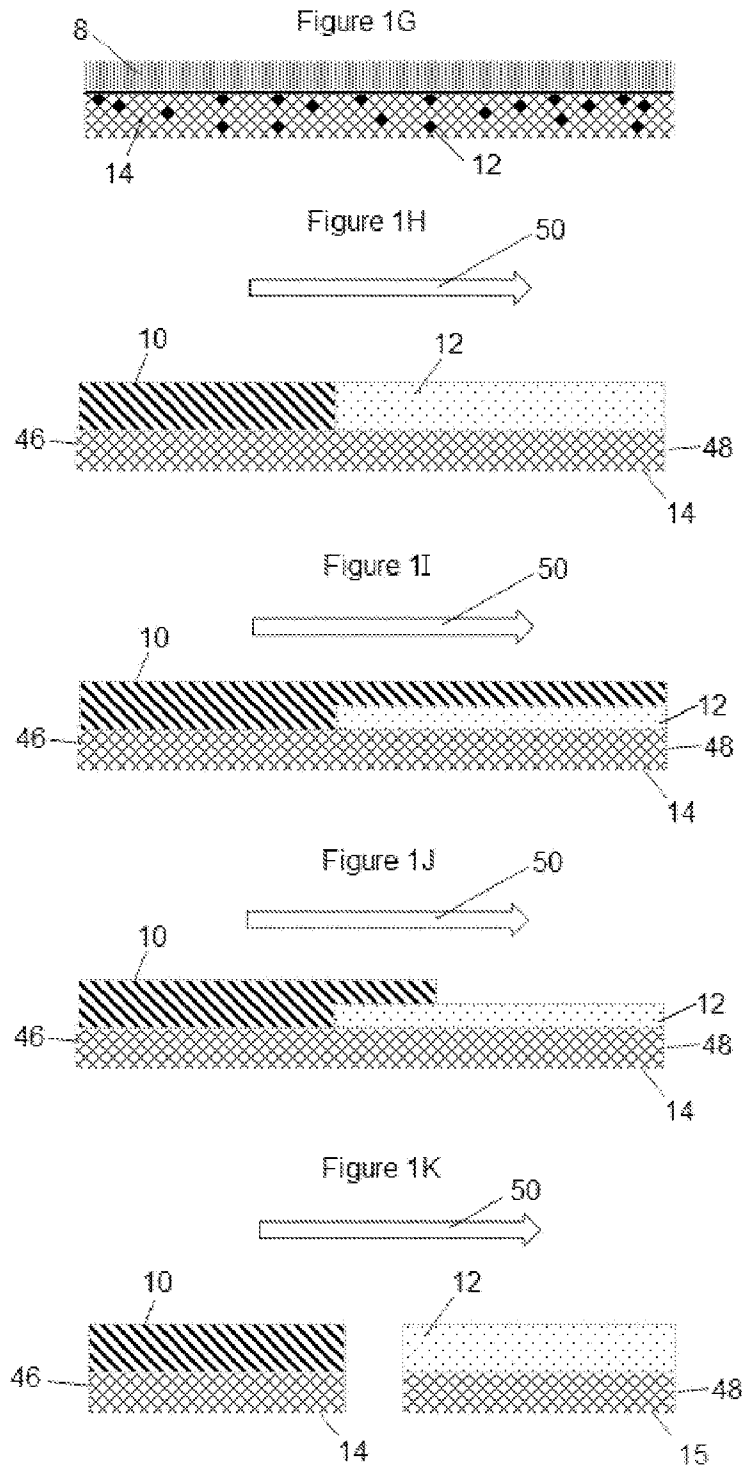
1. Dobbeltlagsammoniakslipkatalysator, der omfatter et SCR-katalysatorlag, et oxidationskatalysatorlag og et substrat, hvor SCR-katalysatorlaget omfatter en molekylsigte eller en vanadium/titanoxid-SCR-katalysator, og
5 oxidationskatalysatorlaget omfatter en oxidationskatalysator, der omfatter mindst ét første metal, som er valgt fra gruppen bestående af kobber (Cu), jern (Fe), cobalt (Co), nikkel (Ni) og chrom (Cr), og et andet metal, som er mangan (Mn), hvor ammoniakslipkatalysatoren ikke omfatter et platingruppermetal, og hvor oxidationslaget er positioneret proksimalt i forhold til substratet.
- 10 2. Dobbeltlagsammoniakslipkatalysator ifølge krav 1, hvor oxidationslaget yderligere omfatter et oxidbæremateriale, der omfatter én eller flere af aluminiumoxid, silica, zirconiumoxid, ceriumoxid og titanoxid.
3. Dobbeltlagsammoniakslipkatalysator ifølge krav 1 eller 2, hvor oxidationslaget omfatter et oxidbæremateriale, der omfatter én eller flere af et
15 stabiliseret aluminiumoxid, silica, zirconiumoxid, ceriumoxid og titanoxid.
4. Dobbeltlagsammoniakslipkatalysator ifølge krav 1, 2 eller 3, hvor oxidationslaget omfatter Cu og Mn.
5. Dobbeltlagsammoniakslipkatalysator ifølge et hvilket som helst af kravene 1 til 4, hvor oxidationslaget yderligere omfatter aluminiumoxid og enten et
20 $\text{CeO}_2/\text{ZrO}_2$ -blandingsoxid eller et Zr-stabiliseret CeO_2 -blandingsoxid.
6. Dobbeltlagsammoniakslipkatalysator ifølge krav 5, hvor det Zr-stabiliserede CeO_2 -blandingsoxid omfatter Ce og Zr, der forekommer i et molforhold på 1:1.
7. Dobbeltlagsammoniakslipkatalysator ifølge et hvilket som helst af kravene
25 2 eller 3, hvor oxidbærematerialet omfatter 20 mol-% La-stabiliseret Al_2O_3 og 80 mol-% Zr-stabiliseret CeO_2 .
8. Dobbeltlagsammoniakslipkatalysator ifølge krav 1, hvor molekylsigten er valgt fra gruppen bestående af MOR (mordenit), FER (ferrierit), FAU (zeolit Y),

MFI (ZSM-5), BEA (beta-zeolitter), Fe-BEA, CHA (chabazit), Cu-CHA og et siliciumaluminiumphosphat, der omfatter en strukturelt lignende ramme.

9. Dobbeltlagsammoniakslipkatalysator ifølge krav 8, hvor SCR-laget omfatter en Fe-BEA- eller en Cu-CHA-zeolit-katalysator eller et siliciumaluminiumphosphat, der omfatter en strukturelt lignende ramme.
10. Dobbeltlagsammoniakslipkatalysator ifølge krav 9, hvor SCR-laget omfatter en Fe-BEA- eller en Cu-CHA-zeolit eller et siliciumaluminiumphosphat, der omfatter en katalysator med en strukturelt lignende ramme, og oxidationslaget omfatter Cu og Mn.
- 10 11. Dobbeltlagsammoniakslipkatalysator ifølge krav 1, hvor katalysatoren i oxidationslaget forekommer i en koncentration på 0,02 til 0,09 g/cm³ (0,3 til 1,5 g pr. tomme³), på basis af den samlede vægt af metal i katalysatoren.
- 15 12. Dobbeltlagsammoniakslipkatalysator ifølge krav 1, hvor katalysatoren i SCR-laget forekommer i en koncentration på 0,03 til 0,15 g/cm³ (0,5 til 2,5 g pr. tomme³), på basis af den samlede vægt af metal i katalysatoren.
13. Dobbeltlagsammoniakslipkatalysator ifølge krav 1, hvor forholdet mellem mængden af katalysator i SCR-laget (i g pr. tomme³) og mængden af katalysator i oxidationslaget (i g pr. tomme³) er mellem 0,3 og 8,3, på basis af den samlede vægt af metal i hvert lag af katalysatoren.
- 20 14. Dobbeltlagsammoniakslipkatalysator ifølge krav 1, hvor SCR-laget er positioneret som et overlæg over oxidationskatalysatoren.
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DRAWINGS





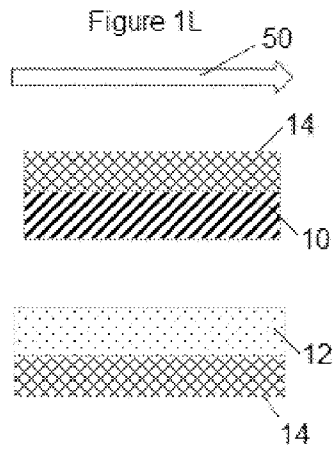


Figure 2: NH₃ Conversion in the Ammonia Slip Catalyst Zone

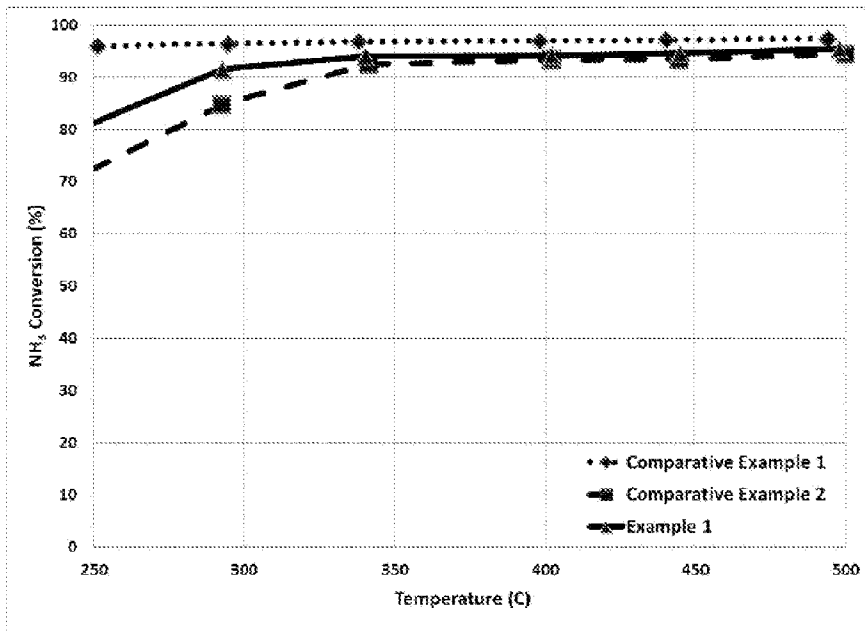


Figure 3: CO Conversion in the Ammonia Slip Catalyst Zone

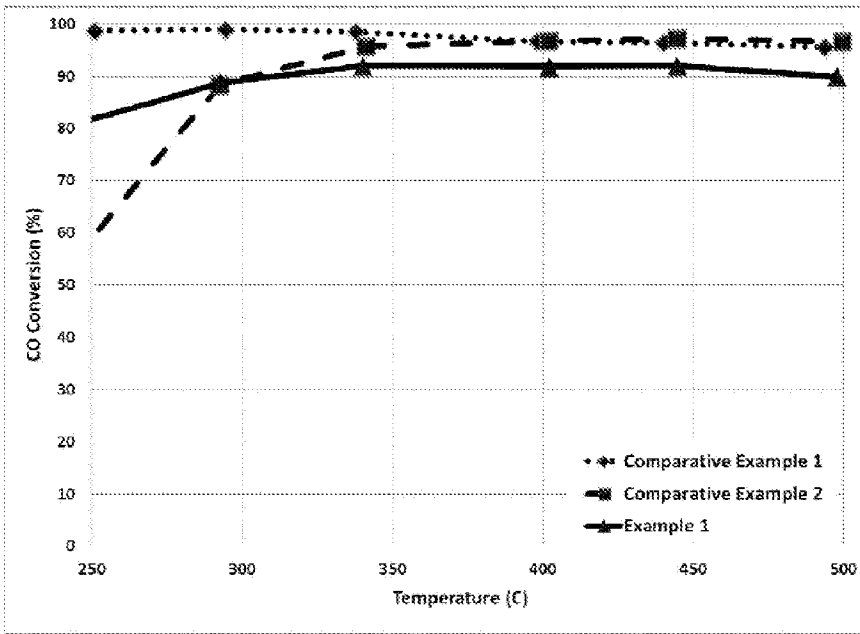


Figure 4: Total System NH₃ + NO_x Output

