Title: ZEOLITE AND REDOX OXIDE COMBINED CATALYST BODY

Abstract: Extruded honeycomb catalyst bodies and methods of manufacturing same. The catalyst body includes a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite.
ZEOLITE AND REDOX OXIDE COMBINED CATALYST BODY

CROSS REFERENCE TO RELATED APPLICATION
[0001] This application claims the benefit of priority to Chinese Patent Application No. 200910118672.1, filed on February 27, 2009.

FIELD
[0002] The present invention relates generally to catalysts and catalyst bodies, such as extruded honeycomb catalyst bodies, such as for use in engine exhaust systems.

BACKGROUND
[0003] Various methods and devices are known for reducing emissions of engine exhaust, including catalyst supports or substrates.

SUMMARY
[0004] The present disclosure relates to catalysts and catalyst bodies, for example extruded honeycomb catalyst bodies, such as for use in engine exhaust systems, and their manufacture.
[0005] In one aspect, the present disclosure relates to a catalyst comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite.
[0006] In another aspect, the present disclosure relates to catalyst structures comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite. The catalyst structure can comprise a body such as an extruded honeycomb catalyst body. In at least some embodiments, the walls of the body are substantially comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite. In some embodiments, the body
comprises one or more layers, such as an external layer; in some of these embodiments, the layer can be the zeolite, or the layer can be a mixture of the first and second oxides, or a mixture of the first and second oxides and the zeolite; and the body may comprise an internal layer of zeolite, a mixture of the first and second oxides, or a mixture of the first and second oxides and the zeolite.

[0007] In one aspect, an extruded honeycomb catalyst body provided in accordance with the present disclosure may be comprised of the first oxide, the second oxide, and a zeolite. In one embodiment, an extruded honeycomb catalyst body provided in accordance with the present disclosure comprises zeolite and WOs-CeO₂-ZrO₂.

[0008] In some embodiments, the extruded honeycomb catalyst bodies of the present disclosure provide a operating temperature window capable of exhibiting the reduction of nitrogen oxide ("NOx") gas in which the temperature at the conversion site is 200°C to 600°C and higher.

[0009] In another aspect, the present disclosure is directed to a method of manufacturing an extruded honeycomb catalyst body comprised of the first and second oxides and the zeolite comprising the steps of (a) forming a mixture of zeolite with the first and second oxides and a binder, (b) extruding the mixture into a cellular body, and (c) firing the cellular body to produce an extruded catalyst body. In some embodiments, the cellular body, as well as the extruded catalyst body, is a honeycomb shaped body.

[0010] In another aspect, the present disclosure is directed to the use of a catalyst or catalytic structure in the treatment of engine exhaust.

[0011] Additional features and advantages of the present disclosure will be set forth in the detailed description which follows, and will be readily apparent to those skilled in the art from that description or recognized by practicing the subject matter as described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0012] It is to be understood that both the foregoing general description and the following detailed description are intended to provide an overview or framework for understanding the nature and character of the inventions as claimed. The accompanying drawings and figures are included to provide a further understanding of the disclosure, and are incorporated into
and constitute a part of the specification. The figures illustrate various embodiments and aspects of the disclosure, and together with the description serve to explain the principles and operations of the claimed invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a graphic illustration comparing NOx gas conversion for pelletized catalyst of W03-Ce02-Zr02 and pelletized catalyst of W03-Ce02-Zr02 mixed with H-ZSM-5 zeolite, as a function of inlet gas temperature.

[0014] FIG. 2A is a graphic illustration of a comparison of the NOx conversion (in %) from an extruded honeycomb made from H-ZSM-5 zeolite (alone), WO3-CeO2-ZrO2 alone plus alumina as a filler, and a mixture of H-ZSM-5 zeolite and WO3-CeO2-ZrO2 at various gas stream temperatures at the inlet to the catalysts, wherein each catalyst was not aged.

[0015] FIG. 2B is a graphic illustration of NOx conversion (in %) for the extruded honeycomb of WO3-CeO2-ZrO2 alone plus alumina as a filler, and the extruded honeycomb of a mixture of H-ZSM-5 zeolite and WO3-CeO2-ZrO2 both aged for 64 hours at 700 °C in 10% steam.

[0016] FIG. 3 is a graphic illustration of NOx gas conversion for pellets made from 0.2g WO3-CeO2-ZrO2 (alone) and for 0.8g WO3-CeO2-ZrO2, physically mixed with 0.2g H-ZSM-5, both pellet sets aged at 700 °C for 4 hours.

[0017] FIG. 4 shows the NOx conversion at different reaction temperatures for the pellet sets of FIG. 3, wherein both pellet sets were aged at 800 °C for 4 hours.

DETAILED DESCRIPTION

[0018] Reference will now be made in detail to the embodiments of the disclosure, examples and aspects of which are illustrated in the accompanying figures.

[0019] In one illustrative embodiment, an extruded honeycomb catalyst body (the "catalyst body") is provided by mixing zeolite with first and second oxides and a binder, the first oxide being selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, and the second oxide being selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof. The mixed
composition can be extruded to form cellular bodies, such as having honeycomb structures, which can be referred to as green bodies, that are then fired to create the catalyst body. In some embodiments, the catalyst body is especially suited in applications for treating engine exhaust streams such as diesel and lean burning engine exhaust containing NO$_x$, HC and ammonia gas.

**[0020]** The first and second oxides and zeolite are stable at automobile exhaust temperatures, exhibit selective catalytic reduction ("SCR"), and can be used with urea injection. These catalysts have NH$_3$ adsorption, NO$_x$ adsorption, and NO$_x$ oxidation sites for optimum NO$_x$ reduction performance. Adsorbed NH3 on the surface interacts with adjacent adsorbed NO$_x$. The NO$_x$ is accordingly reduced to nitrogen and H$_2$O. The zeolite and the first and second oxides exhibit SCR activity of NO$_x$, however, in different temperature ranges. The zeolite (e.g. H-ZSM-5) converts a substantial percentage of NOx at a higher temperature region (e.g. above 400°C, or 500°C, or even 600°C) while the first and second oxides convert a substantial percentage of NOx at a lower temperature region (e.g. below 350°C, or 300°C, or even 250°C). In another aspect, the HC and ammonia gases are also catalytically reduced by the catalyst body.

**[0021]** Combining zeolite with the first and second oxides widens the effective NO$_x$ conversion or reducing temperature window. At least certain embodiments have exhibited an operating temperature window of 200°C to 600°C for the effective reduction of NO$_x$ gas. In contrast, the lower temperature conversion window limit of HZSM-5 zeolite alone is approximately 325°C. Extending the lower window conversion temperature limit may be particularly advantageous for treating engine exhaust such as diesel exhaust gas.

**[0022]** The first and second oxides typically have high surface area (ranging from 20 m$^2$/g to 200 m$^2$/g). One exemplary redox oxide containing both first and second oxides is represented by composition as WOs-CeO$_2$-ZrO$_2$.

**[0023]** Exemplary zeolites include ZSM-5, Beta, Mordenite, Y-zeolite, Ultrastable-Y and aluminum phosphate zeolites, and mixtures thereof. One source of ZSM-5 zeolite is supplied by Zeolyst International of Valley Forge, Pennsylvania, USA. In some embodiments, the zeolite material can have a pore diameter ranging from 0.5 nm to 0.7 nm. In some embodiments, the zeolite has a Si/Al ratio of 15 to 100, or in other embodiments 15 to 50, or
in other embodiments 15 to 30. In one set of embodiments of the present disclosure, a NOx reducing catalyst is comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite. In some embodiments, the catalyst comprises an oxide of Ce, an oxide of W, an oxide of La, or mixtures thereof. In some embodiments, the catalyst comprises an oxide of Zr. In some embodiments, the catalyst comprises an oxide of Ce. In some embodiments, the catalyst comprises an oxide of W. In some embodiments, the catalyst comprises WO3-CeO2-ZrO2. In some embodiments, the catalyst comprises an oxide of W and an oxide of Ce. In some embodiments, the catalyst comprises an oxide of Zr, an oxide of W, and an oxide of Ce. In some embodiments, the catalyst comprises an oxide of W, an oxide of Ce, or a mixture thereof.

[0024] In some embodiments, the catalyst reduces NOx gas by at least 30% at a temperature of 200°C or more. In some of these embodiments, the catalyst reduces NOx gas by at least 30% at a temperature of 200°C to 600°C.

[0025] In some embodiments, at least part of the catalyst is in the form of a honeycomb body comprising a matrix of walls.

[0026] In some embodiments, the zeolite is selected from the group consisting of ZSM-5, beta-zeolites, mordenite, Y-zeolites, ultrastabilized Y-zeolites, aluminum phosphate zeolites, and mixtures thereof.

[0027] In another set of embodiments of the present disclosure, a catalytic structure is comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite. In some embodiments, the catalytic structure is substantially free of platinum, palladium, and rhodium.

[0028] In some embodiments, the structure comprises a body having a plurality of walls defining a plurality of parallel channels. In some embodiments, the body is honeycomb shaped.
In some embodiments, the body comprises an external layer comprised of a mixture of the first and second oxides; in some of these embodiments, the external layer is comprised of a tungsten oxide, a cerium oxide and a zirconium oxide; in other embodiments, the body comprises an external layer comprised of the zeolite.

In some embodiments, the walls of the body are substantially comprised of the zeolite. In some of these embodiments, the walls of the core are coated with a layer of a mixture of a cerium oxide, a zirconium oxide, and a tungsten oxide.

In some embodiments, the walls of the body are substantially comprised of a mixture of the first and second oxides and the zeolite. In some of these embodiments, the walls of the body are formed from extrusion of the mixture.

In some embodiments, the walls of the body are comprised of ceramic, metal, or a combination thereof; in some of these embodiments, the walls of the body are coated with a layer of the zeolite and a layer of a mixture of a cerium oxide, a zirconium oxide, and a tungsten oxide; in some of these embodiments, the layer of zeolite forms an external coating on the walls of the core. In some embodiments, the layer of the mixture forms an external layer on the walls of the core.

In some embodiments, the body is comprised of ceramic or metal. In some of these embodiments, the body comprises ceramic comprised of cordierite, aluminum titanate, mullite, silicon carbide, silicon nitride, or mixtures thereof.

In some embodiments, the structure comprises a tungsten oxide. In some embodiments, the structure comprises an oxide of Zr. In some embodiments, the structure comprises an oxide of Ce. In some embodiments, the structure comprises a cerium oxide, a zirconium oxide, or a combination thereof. In some embodiments, the structure comprises a tungsten oxide and a cerium oxide. In some embodiments, the structure comprises a tungsten oxide, a cerium oxide, and a zirconium oxide. In some embodiments, the structure comprises WO₃-CeO₂-ZrO₂.

In some embodiments, the zeolite is selected from the group consisting of ZSM-5, beta-zeolites, mordenite, Y-zeolites, ultrastabilized Y-zeolites, aluminum phosphate zeolites and mixtures thereof.
In some embodiments, the use of such catalytic structure comprises contacting an exhaust stream containing NOx gas. In some embodiments, the temperature of the exhaust stream is less than 200°C and the NOx gas is catalytically reduced by contact with the structure; in some of these embodiments, the NOx gas is reduced by more than 30%, more than 40%, or even more than 50%. In some embodiments, the temperature of the exhaust stream is greater than 600°C and the NOx gas is catalytically reduced by contact with the structure. In some embodiments, the exhaust stream comprises a reductant (such as ammonia gas or urea) and the reductant is catalytically activated by contact with the structure.

In another set of embodiments of the present disclosure, a catalyst is comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite, wherein the catalyst is capable of reducing NOx gas by at least 30%, in which the temperature of NOx reduction at the conversion site is 200°C to 600°C. In some embodiments, the catalyst comprises an oxide of Ce, an oxide of Zr, and an oxide of W. In some embodiments, the catalyst is formed as an extruded honeycomb body comprising a matrix of walls. In some embodiments, the catalyst comprises WOs-CeO2-ZrO2. In some embodiments, the zeolite is selected from the group consisting of ZSM-5, beta-zeolites, mordenite, Y-zeolites, ultrastabilized Y-zeolites, aluminum phosphate zeolites, and mixtures thereof.

The disclosure may be further understood by reference to the following examples, which are intended to be merely illustrative of the compositions and methods for carrying out the invention.

The catalyst of the present disclosure can be prepared by various procedures, such as coprecipitation (Cop), solution combustion synthesis (SCS), or physical mixing. The catalyst (or catalyst system) can be prepared and its SCR activity (NOx conversion) measured.

FIG. 1 shows the NOx conversion at different reaction temperatures for 1.6g WO3-CeO2-ZrO2 (Cop) (alone) and for 1.3g WO3-CeO2-ZrO2 (Cop), physically mixed with 0.3g H-ZSM-5(Si/Al=17.6, manufactured by Nankai University, Tianjin, China). The reaction conditions were: Im/ catalyst, [NO] = [NH3] = 550 ppm, [O2] = 6%, [CO2] =10%, [H2O] =10%, N2 = balance, total flow rate = 1500 ml/min. It was found that with the addition of
about 25 wt% H-ZSM-5, the high-temperature DeNOx efficiency of WO₃-CeO₂-ZrO₂ (Cop) catalyst was improved significantly (NOx conversion at 600°C increased from 30% to 78%), with substantially the same (only a very small decrease shown in Fig. 1) in the low-temperature DeNOx efficiency. Both catalysts (with and without zeolite ZSM-5) were aged at 700 °C for 4 hours.

[0041] FIG. 2A shows a comparison of the NOx conversion (in %) from an extruded honeycomb made from H-ZSM-5 zeolite (alone), WO₃-CeO₂-ZrO₂ (alone) plus alumina as a filler, and a mixture of H-ZSM-5 zeolite and WO₃-CeO₂-ZrO₂, at various gas stream temperatures at the inlet to the catalysts, wherein each catalyst was not aged. FIG. 2B shows NOx conversion (in %) for the extruded honeycomb of WO₃-CeO₂-ZrO₂ alone plus alumina as a filler, and the extruded honeycomb of a mixture of H-ZSM-5 zeolite and WO₃-CeO₂-ZrO₂, both aged for 64 hours at 700 °C in 10% steam. FIGS. 2A & 2B show the synergetic effect of the mixture of zeolite and WO₃-CeO₂-ZrO₂, which is not found with either of those components alone. Unless otherwise noted, for the extruded honeycomb bodies tested herein, the following conditions applied: 1 inch diameter x 1 inch long honeycombs were produced, and tested at a space velocity of 20,000h⁻¹, with gas flow of 10% O₂, 500 ppmNO, 500 ppm NH₃, 5% H₂O, and the balance N₂.

[0042] FIG. 3 shows the NOx conversion at different reaction temperatures for 1.6g WO₃-CeO₂-ZrO₂ (Cop) (alone) and for 0.8g WO₃-CeO₂-ZrO₂ (Cop), physically mixed with 0.2g H-ZSM-5, both samples aged at 700 °C for 4 hours.

[0043] FIG. 4 shows the NOx conversion at different reaction temperatures for the pellet sets of FIG. 3, wherein both pellet sets were aged at 800 °C for 4 hours. The ceria:zirconia ratio in the above example embodiments was 1:1, in other embodiments, the ceria:zirconia ratio could be in the range of 1:1 to 1:2, inclusive.

[0044] Additional examples of the catalyst body's composition are contained in Table 1 below. The zeolite had a Si/Al ratio of 60. Each body may contain other non-reactive fillers and binders (as superadditions).
Table 1

<table>
<thead>
<tr>
<th>ID</th>
<th>WO₃ (9.1% wt) on CeO₂-ZrO₂ (1:1)</th>
<th>Zeolite %</th>
<th>Alumina</th>
<th>Sample Wt (g)</th>
<th>Cells per square inch/web thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>------</td>
<td>100</td>
<td>------</td>
<td>3.44</td>
<td>200/12</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>------</td>
<td>40</td>
<td>12.53</td>
<td>400/7</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>40</td>
<td>------</td>
<td>7.15</td>
<td>400/7</td>
</tr>
</tbody>
</table>

[0045] The firing procedure for firing the green bodies can be achieved with known ovens, such as periodic (or batch wise) ovens, or kilns, such as tunnel kilns that employ one or more conveyors. In some embodiments, the green bodies can be dried to remove water via microwave or conventional oven wherein the green body is heated to temperatures between 60 to 100 °C. In some embodiments, the green structures are fired by exposing the green structures to a heated gaseous environment, such as air, wherein the air is heated to temperatures in the range of about 100° C-1200° C, and in some of these embodiments between about 500° C-900°C, with a residence time in that temperature range of a duration sufficient to complete firing of the body. The residence time can be about 1 to 48 hours, in some embodiments from 1 to 10 hours, and in some embodiments from 3 to 6 hours, and may depend, for example, on the type or source of components employed.

[0046] In another embodiment, the catalyst body is formed with one or more layers of zeolite and one or more layers of a redox oxide. In one embodiment, the combined zeolite and redox oxide compositions described above are also used in combination with these one or more layers. In a particular embodiment, the zeolite or redox oxide or both are also added as a washcoating layer to the body.

[0047] The catalyst bodies are produced by mixing batch materials, blending the mixture, forming a green body, and subsequently sintering or firing the green body to a hard porous structure. A batch mixture suitable for extrusion can be prepared by mixing the components described above with a suitable liquid vehicle. The vehicle may comprise water and extrusion aids necessary to give the batch plastic formability and sufficient green strength after forming to resist breakage prior to firing. Various lubricants, binders, surfactants, and viscosity modifiers can be added to the batch during the mixing step to provide viscosity control, plasticity, and strength prior to firing, to the fired structure.
The binder component holds the body together to achieve strong mechanical structure for the body. Suitable binder materials include silica or silica forming materials. Mixtures or combinations of binder materials may also be used. The binder is preferably selected from silicone binding agents such as silicone resins and/or emulsions. These can be provided as precursors, for example, silica precursors such as silicone resin, or colloidal silica are suitable. Preferably, the binder is incorporated in the form of a silicone resin or silicone emulsion. Silicone resins can be added to the mixture in the form of an aqueous emulsion, and are commercially available, such as Wacker AG SILRES® M 50 E (an emulsion of a methyl silicone resin with reported solids content of 52%-55%) or Wacker AG SILRES® M 97 E, both available from Wacker-Chemie GmbH of Munich, Germany. In some embodiments, the binder is incorporated in the batch mixtures such that the fired ceramic contains silica binder in an amount ranging from about 5% to about 30% by weight, preferably 15%-30%, and more preferably about 20%. The amounts of the binders are based on the expected weight after heat-treatment which will be the weight of the binder in the product body. For example, when silicone resins are used the weight of the binder in the product is the weight of silica added via the resins. During firing, silica, which may be provided in the form of one or more silica forming materials or in the form of silica itself, softens and propagates throughout the body. Upon cooling after firing, the silica hardens and serves as a binder for the other materials that make up the body.

The extrusion aids will normally comprise both binders and plasticizers/paste formers, as well as processing aids such as lubricants. The plasticizers/paste formers provide plasticity during forming, and some strength to the extruded body prior to firing. Organic pastes suitable for the purposes set forth herein include cellulose ether type materials and/or their derivatives. Sources of cellulose ethers and/or derivatives thereof include the Methocel™ line of cellulose ethers, from Dow Chemical Co., and mixtures thereof. Methylcellulose is an example of an organic paste forming agent suitable for use in formulating the extruded bodies of the present disclosure. The binder, organic paste and other processing aids are generally added as a super addition over the combined weight of the primary phase and secondary phase (based on expected weight after heat treatment). The super addition of organic paste is generally in the range of about 3%-8%, but more or less may be utilized. The organic paste
or temporary binder material is substantially burned off during the subsequent firing of the honeycomb body. Water may be added to the batch components to achieve the necessary plasticity for handling and extrusion. Water-based binders can be used for ease of processing in this regard.

[0050] One method of forming the honeycomb structure is by extrusion through a forming die. A ram extruder, continuous auger, or twin screw extruder or other known extrusion apparatus can be used. The honeycomb body according to the present disclosure can have any convenient size and shape, for example, a right circular cylindrical shape structure. The honeycomb body can be extruded to form a matrix of walls wherein the primary phase material(s), secondary phase material(s) (if present) and permanent binder are generally homogenously distributed throughout the walls. The matrix of walls define channels extending through the honeycomb body. The honeycomb body can be further coated with a skin cement material at the outer periphery of the structure.

[0051] In some embodiments, the catalyst body can have an improved thermo-mechanical durability and improved thermal shock resistance due to a net balance or lowering of the coefficient of thermal expansion ("CTE") resulting from the mixture of zeolite with the first and second oxides. Thermal shock resistance depends on the CTE. The closer the CTE is to zero, the more thermally shock resistant is the material. Zeolites typically have low or negative CTEs, that is, a CTE of -20x10⁻⁶/°C, or even lower over their useful stable temperature ranges. The redox oxides typically have higher CTE than the zeolite. The catalyst body has a higher CTE than a body made from zeolite materials not combined with redox oxides. The redox oxide having a positive CTE balances the negative CTE of the zeolite. Thus, the present disclosure potentially provides thermally shock resistant zeolite-based honeycomb bodies and methods of making them.

[0052] Embodiments of the extruded and fired honeycomb bodies of the present disclosure can be particularly suited for use with engine exhaust systems as flow through substrates. In some embodiments, the provided body is also washcoated with a catalyst material. However, the honeycomb bodies of the present disclosure preferably exhibit high surface area and low thermal expansion, and in some embodiments reduce or eliminate the need for excessive high surface area washcoating.
In some embodiments, the honeycomb body is a flow through substrate.

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

1. A NO\textsubscript{x} reducing catalyst comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite.

2. The catalyst of Claim 1 wherein the catalyst comprises an oxide of Ce, an oxide of W, an oxide of La, or mixtures thereof.

3. The catalyst of Claim 1 wherein the catalyst comprises an oxide of Zr.

4. The catalyst of Claim 1 wherein the catalyst comprises an oxide of Ce.

5. The catalyst of Claim 1 wherein the catalyst comprises an oxide of W.

6. The catalyst of Claim 1 wherein the catalyst comprises WOs-CeO\textsubscript{2}-ZrO\textsubscript{2}.

7. The catalyst of Claim 1 wherein the catalyst comprises an oxide of W and an oxide of Ce.

8. The catalyst of Claim 1 wherein the catalyst comprises an oxide of Zr, an oxide of W, and an oxide of Ce.

9. The catalyst of Claim 1 wherein the catalyst comprises an oxide of W, an oxide of Ce, or a mixture thereof.

10. The catalyst of Claim 1 wherein the catalyst reduces NO\textsubscript{x} gas by at least 30% at a temperature of 200\textdegree{}C to 600\textdegree{}C.
11. The catalyst of Claim 1 wherein the catalyst reduces NO$_x$ gas by at least 30% at a temperature of greater than or equal to 200°C.

12. The catalyst of Claim 1 wherein at least part of the catalyst is in the form of a honeycomb body comprising a matrix of walls.

13. The catalyst of Claim 1, wherein the zeolite is selected from the group consisting of ZSM-5, beta-zeolites, mordenite, Y-zeolites, ultrastabilized Y-zeolites, aluminum phosphate zeolites, and mixtures thereof.

14. A catalytic structure comprising a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite.

15. The catalytic structure of Claim 14 wherein the catalytic structure is substantially free of platinum, palladium, and rhodium.

16. The catalytic structure of Claim 14 wherein the structure comprises a body having a plurality of walls defining a plurality of parallel channels.

17. The catalytic structure of Claim 16 wherein the body is honeycomb shaped.

18. The catalytic structure of Claim 16 wherein the body comprises an external layer comprised of a mixture of the first and second oxides.

19. The catalytic structure of Claim 18 wherein the external layer is comprised of a tungsten oxide, a cerium oxide and a zirconium oxide.
20. The catalytic structure of Claim 18 wherein the body comprises an external layer comprised of the zeolite.

21. The catalytic structure of Claim 16 wherein the walls of the body are substantially comprised of the zeolite.

22. The catalytic structure of Claim 21 wherein the walls of the core are coated with a layer of a mixture of a cerium oxide, a zirconium oxide, and a tungsten oxide.

23. The catalytic structure of Claim 16 wherein the walls of the body are substantially comprised of a mixture of the first and second oxides and the zeolite.

24. The catalytic structure of Claim 23 wherein the walls of the body are formed from extrusion of the mixture.

25. The catalytic structure of Claim 16 wherein the walls of the body are comprised of ceramic, metal, or a combination thereof.

26. The catalytic structure of Claim 25 wherein the walls of the body are coated with a layer of the zeolite and a layer of a mixture of a cerium oxide, a zirconium oxide, and a tungsten oxide.

27. The catalytic structure of Claim 26 wherein the layer of zeolite forms an external coating on the walls of the core.

28. The catalytic structure of Claim 26 wherein the layer of the mixture forms an external layer on the walls of the core.

29. The catalytic structure of Claim 16 wherein the body is comprised of ceramic or metal.
30. The catalytic structure of Claim 29 wherein the body comprises ceramic comprised of cordierite, aluminum titanate, mullite, silicon carbide, silicon nitride, or mixtures thereof.

31. The structure of claim 14 wherein the structure comprises a tungsten oxide.

32. The method of claim 14 wherein the structure comprises an oxide of Zr.

33. The method of claim 14 wherein the structure comprises an oxide of Ce.

34. The structure of claim 14 wherein the structure comprises a cerium oxide, a zirconium oxide, or a combination thereof.

35. The structure of claim 14 wherein the structure comprises a tungsten oxide and a cerium oxide.

36. The structure of claim 14 wherein the structure comprises a tungsten oxide, a cerium oxide, and a zirconium oxide.

37. The structure of claim 14 wherein the structure comprises WO₅-CeO₂-ZrO₂.

38. The structure of claim 14 wherein the zeolite is selected from the group consisting of ZSM-5, beta-zeolites, mordenite, Y-zeolites, ultrastabilized Y-zeolites, aluminum phosphate zeolites and mixtures thereof.

39. The use of the catalytic structure of claim 14 comprising contacting an exhaust stream containing NOₓ gas.
40. The use of Claim 39 wherein the temperature of the exhaust stream is less than 200°C and the NO\textsubscript{x} gas is catalytically reduced by contact with the structure.

41. The use of Claim 39 wherein the temperature of the exhaust stream is greater than 600°C and the NO\textsubscript{x} gas is catalytically reduced by contact with the structure.

42. The use of claim 39 wherein the exhaust stream comprises a reductant and the reductant is catalytically activated by contact with the structure.

43. A catalyst comprised of a first oxide selected from the group consisting of tungsten oxides, vanadium oxides, and combinations thereof, a second oxide selected from the group consisting of cerium oxides, lanthanum oxides, zirconium oxides, and combinations thereof, and a zeolite, wherein the catalyst is capable of reducing NO\textsubscript{x} gas by at least 30%, in which the temperature of the NO\textsubscript{x} gas is 200°C to 600°C.

44. The catalyst of claim 43 wherein the catalyst comprises an oxide of Ce, an oxide of Zr, and an oxide of W.

45. The catalyst of claim 43 formed as an extruded honeycomb body comprising a matrix of walls.

46. The catalyst of claim 43 wherein the catalyst comprises WOs-CeO\textsubscript{2}-ZrO\textsubscript{2}.

47. The catalyst of claim 43, wherein the zeolite is selected from the group consisting of ZSM-5, beta-zeolites, mordenite, Y-zeolites, ultrastabilized Y-zeolites, aluminum phosphate zeolites, and mixtures thereof.

48. The catalyst of Claiml wherein the catalyst comprises ceria and zirconia in a ratio of 1:1 to 1:2.
49. The catalytic structure of Claim 14 wherein the catalytic structure comprises ceria and zirconia in a ratio of 1:1 to 1:2.

50. The catalyst of Claim 43 wherein the catalyst comprises ceria and zirconia in a ratio of 1:1 to 1:2.
FIG. 2A

Inlet Temperature °C

FIG. 2B

Inlet Temperature °C
INTernational Search Report

A. CLASSIFICATION OF SUBJECT MATTER

BE01D53/94 BE01J23/10 BE01J23/16 BE01J29/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

BO01D BO01J

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>DE 198 06 062 A1 (SIEMENS AG [DE]) 19 August 1999 (1999-08-19) the whole document</td>
<td>1,14,39,43</td>
</tr>
</tbody>
</table>

Date of the actual completion of the international search: 29 April 2010

Date of mailing of the international search report: 18/05/2010

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

Authorized officer:
Polesak, Helmut
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>US 2005101473 A1</td>
<td>12-05-2005</td>
</tr>
<tr>
<td>DE 19806062 A1</td>
<td>19-08-1999</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 8028000 A</td>
<td>17-09-2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 2000280280 B2</td>
<td>23-12-2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BR 0017155 A</td>
<td>20-04-2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2401004 A1</td>
<td>13-09-2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 60036414 T2</td>
<td>12-06-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1264083 A1</td>
<td>11-12-2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ES 2292477 T3</td>
<td>16-03-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2003526042 T</td>
<td>02-09-2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 0166918 A1</td>
<td>13-09-2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2003221360 A1</td>
<td>04-12-2003</td>
</tr>
</tbody>
</table>