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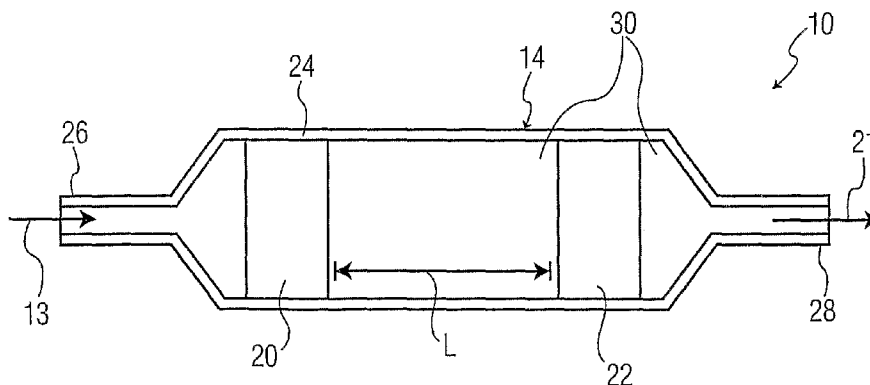
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(54) Title: METHOD AND APPARATUS FOR REDUCING NOX WITH FIRST AND SECOND CATALYSIS



(57) Abstract: A method and apparatus; (10) for catalytically processing a gas stream (13) passing therethrough to reduce the presence of NO therein, wherein the apparatus includes a first catalyst (20) composed of a silver containing alumina that is adapted for catalytically processing the gas stream at a first temperature range, and a second catalyst (22) composed of a copper containing zeolite located downstream from the first catalyst, wherein the second catalyst is adapted for catalytically processing the gas stream at a lower second temperature range relative to the first temperature range.

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METHOD AND APPARATUS FOR COMBINATION CATALYST FOR REDUCTION
OF NO_x IN COMBUSTION PRODUCTS

Field of the Invention

The present invention relates generally to methods and apparatus for removing pollutant gases from the exhaust gas stream formed by a combustion process such as required in the operation of internal combustion engines, furnaces, power plants, and so forth, and is more particularly related to catalysts used in removing nitrogen oxide (NO_x) from the exhaust gases resulting from a combustion process.

Background of the Invention

A continuing effort has been made over the years for developing methods and systems for removing pollutant gases from exhaust gases produced by combustion equipment. In recent years, environmental regulations have been made law in numerous countries around the world in an effort to reduce the emission of pollutant gases into the atmosphere from combustion equipment. Of major concern is the production of nitrogen oxides (NO_x) by motor vehicles driven by internal combustion

production of nitrogen oxides (NO_x) by motor vehicles driven by internal combustion engines, such as gasoline driven engines, and particularly diesel engines. Other combustion apparatus are also of concern, such as furnaces installed in factories, commercial and home heating devices, power plant equipment, and so forth.

5

During the combustion process in such equipment when nitrogen in the air reacts with oxygen within a combustion chamber, under the high temperature and pressure conditions that typically exist therein, such as in the cylinder of an internal combustion engine, nitrogen oxides (NO_x) are produced, which typically include
10 either one or a combination of nitrogen monoxide and nitrogen dioxide, commonly referred to as NO_x emissions. The NO_x emissions are major atmospheric pollutants that cause smog, and acid rain. The major industrialized countries throughout the world have instituted regulations for reducing NO_x emissions.

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As a result, a major effort has been ongoing over an extended period of time for developing methods and systems to substantially eliminate the emission into the atmosphere of nitrogen oxides or NO_x via exhaust gas streams from combustion equipment. Recognizing that automobile emissions are a major source of air
20 pollution, in the 1966 automobile model year, the state of California passed regulations requiring the use of exhaust emission control systems in vehicles sold in California. Similar regulations were instituted throughout the United States by automotive model year 1968.

In combustion processes, the "perfect mixture" of a fuel and air is referred to in thermodynamics by the term "stoichiometric." This is the point at which the amount of air is just enough to combust all of the fuel, with no excess oxygen remaining. For many reasons, internal combustion engines cannot be run stoichiometrically, and are typically run lean, where there is an excess of oxygen to fuel relative to the stoichiometric condition. Although both gasoline and diesel internal combustion engines are typically run as lean-burn engines, such a condition is most often found in operating diesel engines, and leads to the emission of undesirable amounts of NO_x in the exhaust gases from such engines. At times engines may run rich, that is with an excess of fuel relative to oxygen. Note that for gasoline, the stoichiometric mixture is 14.6:1. Even under these conditions, some nitrogen from the air can react with oxygen to form NO_x

The exhaust gas stream from lean-burn engines contain significant amounts of oxygen, thereby preventing the efficient removal of NO_x from the gas stream through use of conventional exhaust catalysts such as a "3-Way Catalyst." As a result, NO_x trap or NO_x storage/reduction systems have been developed to assist in removing NO_x from current lean-burn engines. However, these systems must rely on close engine control for alternating between rich and lean conditions in the exhaust gas stream. During the lean phases, the catalyst employed stores NO_x. During the rich phases, the catalyst reduces NO_x to N₂. Also, HC-SCR systems have been developed as retrofits for use in reducing NO_x from the exhaust gas stream of internal combustion engines, but such systems have found only limited use.

Accordingly, there is a need in the art for improved methods and apparatus for removing NO_x from the exhaust gas stream of a combustion device, such as internal combustion engines.

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Summary of the Invention

The present invention relates to a method and apparatus for catalytically processing a gas stream to remove or at least substantially reduce NO_x compounds therefrom. The apparatus of the present invention provides an efficient means for reducing or eliminating NO_x compounds in exhaust gases produced by an internal combustion engine. In particular, the apparatus of the present invention efficiently processes the exhaust gases from lean-burn engines such as diesel engines, for example, whose exhaust gases exhibit a relatively large proportion of oxygen content.

10 The present invention makes use of a combination of a first catalyst that exhibits NO_x conversion activity at a relatively high temperature with a second catalyst that exhibits at least similar activity at a lower temperature to yield a synergistic result. The present invention is characterized by a broader temperature range of operation and enhanced gas stream processing capacity. More particularly, the present invention makes use of

15 catalyst combinations that result in a synergistic effect, better than the sum of the parts by producing the correct set of intermediate nitrogen compounds on the first catalyst, and reducing these over the second catalyst.

20

The apparatus of the present invention comprises generally a first catalyst adapted to operate at an optimal first temperature, and a second catalyst adapted to operate at a lower optimal second temperature relative to the first temperature. The first catalyst is positioned upstream from the second catalyst in a manner which enables the exhaust gases in the form of a gas stream to flow from the first catalyst to the second catalyst. The first and second catalysts may be arranged immediately one after another or in a spaced-apart relationship.

In one embodiment of the present invention, a reductant generally in the form of a hydrocarbon compound is introduced into the gas stream to further enhance the NO_x removal activity of the apparatus via hydrocarbon-selective catalytic reduction (HC-SCR).

In a preferred embodiment of the present invention, the first catalyst is composed of a metal containing alumina material, and the second catalyst is composed of a metal containing zeolite material. During operation, the exhaust gases are passed through the apparatus and sequentially processed by the first and second catalysts. The first and second catalysts, in combination, operate to remove or at least substantially reduce the NO_x compounds and convert them into environmentally compatible by-products in a simple, cost efficient manner.

In one aspect of the present invention, there is provided an apparatus for catalytically processing a gas stream passing therethrough to reduce the presence of NO_x therein, the apparatus comprising:

a first catalyst having a first optimal processing temperature range for catalytically
5 processing the gas stream; and

a second catalyst located downstream from the first catalyst, said second catalyst having a second lower optimal processing temperature range relative to the first temperature range for catalytically processing the gas stream subsequent to the first catalyst.

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In a particular aspect of the present invention, there is provided an apparatus for catalytically processing a gas stream passing therethrough to reduce the presence of NO_x therein, the apparatus comprising:

a first catalyst comprising metal containing alumina, said first catalyst having a
15 first optimal processing temperature range for catalytically processing the gas stream;
and

a second catalyst comprising metal containing zeolite located downstream from
the first catalyst, said second catalyst having a second lower optimal processing
temperature range relative to the first optimal processing temperature range for
20 catalytically processing the gas stream subsequent to the first catalyst.

In another aspect of the present invention, there is provided a method for catalytically processing a gas stream to reduce the presence of NO_x therein, said

method comprising:

delivering the gas stream to a first catalyst having a first optimal processing temperature range for catalytically processing the gas stream; and

conveying the gas stream from the first catalyst to a second catalyst, wherein
5 said second catalyst has a lower second optimal processing temperature range relative to the first optimal processing temperature range for catalytically processing the gas stream subsequent to the first catalyst.

Brief Description of the Drawings

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Various embodiments of the invention are described in detail below with reference to the drawings, in which like items are identified by the same reference designation, wherein:

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Figure 1 is a schematic diagram illustrating the application of an apparatus for catalytically processing a gas stream to remove or at least substantially reduce NO_x compounds therefrom, and adapted for use with a diesel engine in accordance with one embodiment of the present invention;

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Figure 2 is a longitudinal cross sectional view of an apparatus for catalytically processing a gas stream to remove or at least substantially reduce NO_x compounds therefrom in accordance with one embodiment of the present invention;

Figure 3 is a graph comparing the performance of the combination of Ag/Alumina and Cu/ZSM-5 catalysts to the performances of the catalysts individually in accordance with the present invention in the absence of water;

5 Figure 4 is a graph comparing the performance of the combination of Ag/Alumina and Cu/ZSM-5 catalysts to the performances of the catalysts individually in accordance with the present invention in the presence of water;

10 Figure 5 is a graph comparing the performances of the combination of Ag/Alumina and Cu/ZSM-5 catalysts at different copper loadings in accordance with the present invention;

15 Figure 6 is a graph comparing the performance of the combination of Ag/Alumina and Cu/ZSM-5 catalysts to the performances of the catalysts individually in the presence of a dodecane reductant in accordance with the present invention;

20 Figure 7 is a graph comparing the performance of the combination of Ag/Alumina and Cu/ZSM-5 catalysts in different physical arrangements in accordance with the present invention; and

Figure 8 is a graph comparing the performance of the combination of Ag/Alumina and Cu/ZSM-5 catalysts to the performance of the combination of Ag/Alumina and Pt/Alumina catalysts in accordance with the present invention.

Detailed Description of the Invention

The present invention is directed to method and apparatus for catalytically
5 processing a gas stream to remove or at least substantially reduce NO_x compounds
therefrom. The apparatus and method of the present invention provides an efficient
means for reducing or eliminating NO_x compounds in exhaust gases produced from an
internal combustion engine. The apparatus and method of the present invention is
designed to promote the catalytic conversion of NO_x compounds present in the exhaust
10 gases into environmentally compatible products. The apparatus of the present invention
has been observed to yield a synergistic effect utilizing a combination of first and second
catalysts in the presence of a reductant generally in the form of a hydrocarbon, while
using minimal packaging space. It is envisioned that the apparatus disclosed herein is
suitable for use in lean NO_x exhaust aftertreatment systems.

15

The present invention is designed to promote a synergistic effect from the
combination of different catalysts by tailoring the intermediate reactant species,
producing ammonia, amines, nitriles and other organo-nitrogen species. The present
invention is capable of generating higher NO_x reduction performance, while maintaining
20 the same packaging volume and space velocity.

Referring to Figure 1, a schematic diagram showing an apparatus of the present
invention identified by reference numeral 10 coupled to a "lean burn" engine 12 in the

form of a diesel engine. As used herein, a "lean burn engine" is defined as one that produces an oxygen-rich exhaust, which is defined as an exhaust having a higher molar ratio of oxygen than the total molar ratio of reductive compounds such as CO, hydrogen and hydrocarbons. The exhausts have an oxidative environment. Examples of such engine systems include diesel engine systems, spark ignited natural gas or alternative fuel engine systems, liquid or gaseous fueled turbine engines, and various lean burn gasoline engine systems. Generally, diesel engine systems, as shown in Figure 1 generate an exhaust having an oxygen content of from 4% to 16% depending on the load conditions and the running mode of the diesel engine.

10

An oxygen rich exhaust 13 exits engine 12 and is directed to the apparatus 10. Preferably, this exhaust is supplemented by the addition of a reductant in the form of an atomized hydrocarbon or mixture of hydrocarbons 18. In the illustrated embodiment, one source of these hydrocarbons can be the diesel fuel 15 in a tank 2 used as the primary source of fuel for the diesel engine 12. The hydrocarbon reductants can be the residual hydrocarbons remaining in the exhaust after the combustion event during an engine cycle. Alternatively, the supplemental hydrocarbons can be introduced as a post injection event, preferably during the power stroke or exhaust stroke of a four stroke diesel engine. Yet another alternative, as illustrated, is to introduce the supplemental hydrocarbon in the exhaust system at a location downstream of the engine cylinders using an auxiliary injector 17 controlled by the engine control module (ECM) 19. It is also well known to use hydrocarbons other than the primary diesel fuel.

20

The engine exhaust is directed to the apparatus 10 comprising a catalytic unit 14. Deposited within the catalytic unit 14 is a combination of metal containing catalysts having the customized physical and chemical characteristics disclosed herein, that yield both high NO_x removing performance, as well as other advantageous lean NO_x catalyst performance characteristics. The composition of the combination of metal containing catalysts as well as the catalytic reactions is described in greater detail below.

Referring to Figure 2, the apparatus 10 includes a catalytic unit 14 which is placed downstream from the lean burn engine 12 along the outgoing exhaust pipe 16. The exhaust 13 in the form of a gas stream (represented by an arrow) from the engine 12 is conducted along the exhaust pipe 16 in the direction indicated by the associated arrow in Figure 2. For one embodiment of the present invention, the apparatus 10 includes an airtight housing 24 defining a packaging volume 30 occupied by the catalytic unit 14, an inlet port 26 at one end, and an outlet port 28 at the opposed end thereof. The packaging volume 30 is in fluid communication between the inlet and outlet ports 26 and 28, respectively. The inlet port 26 supplies the exhaust 13 from the combustion engine, and the outlet port 28 discharging an outgoing, purified exhaust gas stream 21.

The catalytic unit 14 of the apparatus 10 includes a first catalyst 20 having a first optimal processing temperature range for catalytically processing the gas stream of the exhaust 13, and a second catalyst 22 located downstream from the first catalyst 20. The second catalyst 22 exhibits a second lower optimal processing temperature range relative to the first temperature range for catalytically processing the gas stream

subsequent to the first catalyst 20. In particular, the first catalyst 20 is adapted to facilitate the reaction of NO_x with hydrocarbons to yield nitrogen-containing intermediates such as amines, ammonia, organo-nitrogen species and oxygenates. These intermediate species desorb into the gas phase along with activated NO_x species. The second catalyst 22 is adapted to facilitate the reaction of these intermediates for further reduction into N₂. The inventors believe the first catalyst not only converts some of the NO_x directly to N₂, but also produces intermediate species from the remaining NO_x that further react to form N₂ over the second catalyst.

10 In a preferred embodiment of the present invention, the first catalyst 20 is composed of a catalytically active metal-containing alumina (Al₂O₃) material, preferably a metal-containing γ -alumina material, and the second catalyst 22 is composed of a catalytically active metal-containing zeolite material, preferably a metal-containing ZSM-5 material. The first and second catalysts 20 and 22 are generally structurally arranged
15 into catalyst beds which may be in the form of powders, pellets, particles, washcoated or formed monoliths such as a honeycomb structure, and the like.

The metal of the first catalyst 20 is preferably selected from silver, indium, gallium, tin, cobalt, and mixtures thereof, and more preferably from silver. The loading
20 of the metal of the first catalyst 20 is preferably from about 1 to 15 wt% based on the total weight of the first catalyst, and more preferably from about 2 to 5 wt%. With the use of a reductant in the exhaust 13, a metal loading of at least 2% is preferred. In a

preferred embodiment of the present invention, the first catalyst 20 is composed of silver-containing alumina catalyst (Ag/alumina).

It has been found that alumina formed by a sol-gel method produces a material
5 having unique properties for utilization in lean NO_x catalytic treatment of oxygen rich exhaust. Various methods of forming the alumina component were investigated. In one embodiment, γ -alumina was prepared by a complexing agent-assisted, sol-gel method. Another embodiment had the γ -alumina support material prepared by sol-gel method without the use of a complexing agent.

10

The alumina component of the first catalyst 20 is preferably synthesized via sol gel methods using a complexing agent in combination with a washing step employing an alcohol, such as, for example, 2-propanol. The sol gel method is advantageous in that the resulting product is characterized by a basic pH, excellent hydrothermal stability,
15 and optimized metal dispersion on the alumina component to maximize loading capacity and uniformity, thereby enhancing greater reduction of NO_x compared to conventional preparation methods. Specific details on the sol-gel process can be found in Example 2 hereinafter. Further details on the synthesis of alumina via the sol-gel process can be found in U.S. Patents 6,703,343 and 6,706,660, the teachings of which are incorporated
20 herein by reference to the extent they do not conflict herewith.

The metal doping or loading of the alumina material is preferably accomplished in one of two ways. In one method, the subject metal dopant is solubilized in the water that is used to stop gelation during the sol-gel procedure described above.

5 In a second method, the calcined sol-gel γ -alumina is doped with a metal by an incipient wetness impregnation method. In the preferred incipient wetness impregnation method, the calcined powder sol-gel prepared γ -alumina is brought into contact with a solution of the appropriate metal. The solution of the metal is present in an amount equal to or greater than the total pore volume of the γ -alumina sample. The pore
10 volume of γ -alumina prepared is preferably between about 0.5 and about 2.0 cc/g of alumina.

To form an indium or indium oxide doped γ -alumina by the incipient wetness method an appropriate amount of $\text{In}(\text{NO}_3)_3$ (or InCl_3) is dissolved in a water solution and
15 brought into contact with the sol-gel γ -alumina. The indium or indium oxide doped γ -alumina catalyst is then calcined at 600°C for about 5 hours.

Tin or tin oxide doped γ -alumina is prepared in the same manner using SnCl_3 in an ethanol solution instead of water. The tin or tin oxide doped γ -alumina catalyst is
20 calcined at 600°C for about 5 hours and then at 800°C. for about 2 hours.

A third promising metal promoter evaluated is gallium or gallium oxide. A gallium or gallium oxide doped γ -alumina is prepared by exposing the γ -alumina to a water

solution of $\text{Ga}(\text{NO}_3)_3 - \text{H}_2\text{O}$ which is added to the aluminum oxide gel during the γ -alumina preparation in the sol-gel method. The gallium or gallium oxide doped γ -alumina catalyst is calcined at 600°C for about 5 hours to form oxides of gallium loaded alumina.

5 The metal of the second catalyst 22 is preferably selected from copper, iron, cobalt, mixtures thereof, and more preferably from copper. The loading of the metal of the second catalyst 22 is preferably from about 2 to 15 wt% based on the total weight of the second catalyst, and more preferably from about 3 to 11.5 wt%. In a preferred embodiment of the present invention, the second catalyst 22 is composed of a copper
10 containing zeolite catalyst (Cu/zeolite). The zeolite component may be selected from any suitable zeolite including, but not limited to, ZSM-5, ZSM-11, ZSM-35, MCM-22, MCM-49, Beta, MCM-56, ITQ-13, and MCM-68. A preferred zeolite is ZSM-5. Further details on metal doping or loading the ZSM-5 component can be found in Example 1 hereinafter.

15

The first and second catalysts 20 and 22 of the catalytic unit 14 are enclosed within the packaging volume 20 of the housing 24 with the first catalyst 20 positioned upstream from the second catalyst 22. The first and second catalysts are present in an amount ratio ranging from about 1:2 to 2:1, with a ratio of about 1:1 being preferred. In
20 this embodiment, the first and second catalysts 20 and 22 are arranged in juxtaposition to one another. Alternatively, the first and second catalysts 20 and 22 are maintained spaced apart at some distance L, from one another. Typically, performance increases as the residence time decreases. The first catalyst 20 in combination with the second

catalyst 22 function to convert and reduce the presence of NO_x in the gas stream of the exhaust 13 entering through the inlet port 26 and exiting out of the outlet port 28 of the apparatus 10 in a more purified form.

5 As discussed above, the exhaust 13 can be injected with a reductant before the catalytic unit 14 to enhance the catalytic reaction associated with converting NO_x to N₂. The reductant can be tapped off the fuel tank 15 associated with the combustion engine 12 and injected into the exhaust 13 via a fuel injector or other suitable means. Other examples of suitable reductants in association with a diesel engine include dodecane,
10 ethanol, propane, diesel fuel, kerosene, diesel-range paraffins, diesel-range non-aromatic streams, and the like. Other examples of suitable reductants in association with a gasoline engine include gasoline, propane, ethanol, octane, and the like.

EXAMPLE 1

15

A sample of copper containing ZSM-5 zeolite catalyst was produced by preparing a solution containing 68 grams of copper (II) nitrate hydrate and 1000 ml of deionized water. Thereafter, 200 grams of ZSM-5 zeolite crystal were added while the solution was stirred. The resulting mixture was stirred for about 1.5 hours and then the pH was
20 adjusted to 7.25 by the addition of 35.7 grams of NH₄OH. The stirring of the mixture continued for about 1 hour. The zeolite mixture was filtered, and washed with 1000 ml of deionized water. The filtrate was dried overnight at about 85°C. The exchanged zeolite was then air calcined by ramping the temperature at a rate of 2°C/min to 550°C,

holding for about 2 hours, and then cooled to room temperature. Copper analysis indicated the copper loading was about 11.5 wt.%.

A sample with 3 weight % copper loading was prepared using the above
5 procedure by varying the amount of copper (II) nitrate hydrate.

EXAMPLE 2

γ -Alumina support was prepared by utilizing a complexing agent-assisted sol gel
10 method. 500 grams of aluminum isopropoxide (AIP) (98%+, Aldrich Chemical Company, Inc.) was dissolved in 600 ml of 2-methyl-2,4-pentanediol (MPD) (99% Aldrich Chemical Company, Inc) in a beaker. The resulting mixture was stirred vigorously with a mechanical polyethylene stirrer. Once the mixture was mixed homogenously, the beaker was placed in a constant temperature bath at a temperature
15 of about 120°C and stirred continuously for about an hour. Once all the AIP was dissolved, a clear yellowish green solution was obtained. The AIP reacts with MPD to yield 2-propanol in the form of a vapor at the 120°C reaction condition and the solution begins to gel. Once the gelation is completed after 4 hours, 400 ml of water was added to terminate the gelation and yield a white precipitate (aluminum hydroxide). The white
20 solid product was redispersed in water and aged at 90°C overnight under constant stirring.

After aging overnight, 600 ml of 2-propanol was added to remove the water from the pores of the precipitate. Although 2-propanol or methanol is preferred, any organic solvent having a surface tension of about equal to or less than 30 mN/m will be useful. It is just necessary that the solvent have a surface tension significantly below that of
5 water, which is about 72 mN/m. The slurry was vacuum filtered and dried at 90°C in an oven for about 48 hours.

Calcination was carried out in a temperature programmed tube furnace with 5L/min air flowing through it. A general calcinations schedule is as follows: ramp the
10 temperature from 100°C to 700°C at about 1°C/min; maintain at 700°C for a prescribed time, and turn off the heat and continue air over the alumina until the temperature is reduced to 100°C. During calcinations, a selected amount of water (e.g., 2% to 6% or more) can be added to partially sinter the powders.

15 This procedure can be controlled so as to yield γ -alumina with pre-aging surface areas greater than about 200 m²/g, pre-aging pore volumes of from about 1.0 to 2.0 cc/g and pre-aging pore sizes averaging from about 4 to 20 nm. The resulting alumina product had a surface area of from about 200 to 230 m²/g.

EXAMPLE 3

Several samples of silver containing γ -alumina catalysts were prepared via the incipient wetness impregnation technique. Aqueous silver nitrate or silver sulfate solution was added drop-wise and mixed with the γ -alumina product of Example 2. The volume of the nitrate solution was calculated to substantially match the pore volume of the γ -alumina product, which was about 1.4 ml per gram of γ -alumina. Thus, 0.322 grams of silver nitrate was dissolved in 14 ml of water and mixed with 10.0 grams of alumina. The impregnated sample was then manually mixed with a spatula, dried overnight at 90-110°C, and calcined for about 5 hours at 600°C in the presence of air. In another preparation, 0.2966 grams of silver sulfate was dissolved in 42 ml of water because of lower solubility, and this was added in three steps using 14 ml each time with drying and calcination between the steps. The silver loading in the catalyst was 2 weight % based on the total weight of the catalyst.

15

EXAMPLE 4

Two catalysts were prepared by dissolving 500g aluminum isopropoxide (AIP) in 600ml 2-methyl-2,4-pentanediol (MPD) using the sol-gel procedure described in Example 2. In this example, however, as part of the preparation, 4.025g Ag(NO₃) or 3.7075g Ag₂(SO₄) was dissolved in 600mL propanol and added to the slurry during the propanol washing step of Example 2. The slurry was mixed for about an hour and the resulting products were vacuum filtered to yield the catalysts.

20

EXAMPLE 5

Catalyst evaluation experiments were conducted in a quartz reactor heated in an electric furnace. A gas mixture was passed over a catalyst bed supported in the quartz reactor. The gas mixture contained 1000 ppm NO (nitric oxide), 1000 ppm propylene as a reductant, and 9% oxygen with the remaining portion composed of helium. The total flow rate of the gas was about 1500 ml/minute, and the catalyst volume was about 3.0 ml to yield a gas hourly space velocity (GHSV) of 30,000. The temperature of the catalyst was increased from 150°C to 550°C and then reduced back to 150°C. Data were recorded as the temperature was reduced. In one evaluation, 1.5 ml of Ag/alumina catalyst was placed upstream of 1.5 ml of Cu/ZSM-5 catalyst. In the second and third evaluations, the catalysts were evaluated individually. The copper loading was about 11.5 wt% based on the total weight of the copper containing catalyst. The alumina catalyst contained 2 wt% silver.

15

As shown in the graph of Figure 3, the results of the evaluations compare the performance of the combination of catalysts to the performances of the catalysts individually. The graph shows that the combination of catalysts as represented by curve 30 exhibited a broader temperature window of activity in removing NO_x when compared to the individual catalysts as represented by curves 32 and 34, respectively.

20

EXAMPLE 6

A catalyst evaluation experiment was conducted in a quartz reactor heated in an electric furnace in accordance to the procedures described in Example 5 except the gas mixture passing over the catalyst bed included 7% water. Further evaluations were made to compare the effects of copper loading at about 3 wt% and about 11.5 wt%, respectively, based on the total weight of the copper containing catalyst.

As shown in the graph of Figure 4, the results of the evaluations compare the performance of the combination of catalysts to the performances of the catalysts individually. The graph shows that the combination of catalysts as represented by curve 36 maintains a broader temperature window of catalytic activity in removing NO_x even in the presence of water than the individual catalysts as represented by curves 38 and 40, respectively.

15

As further shown in Figure 5, catalytic activity at the higher end of the temperature range was observed to be improved with lower Cu loading at about 3 wt% represented by curve 42 as compared to the Cu loading of about 11.5 wt.% based on the total weight of the copper containing catalyst represented by curve 44.

20

EXAMPLE 7

The Ag/alumina and Cu/ZSM-5 catalysts were wash coated onto a 1" diameter by 3" long monolith and evaluated with dodecane (a diesel range molecule) as a reductant.

5 The evaluations were carried out in a quartz reactor heated in an electric furnace. A gas mixture was passed over a catalyst bed supported in the quartz reactor. The gas mixture contained 500 ppm NO (nitric oxide), 3000 ppm dodecane as a reductant, 50 ppm propene, 500 ppm CO, 8% carbon monoxide, 7% water, and 9% oxygen with the remaining portion composed of helium. The gas hourly space velocity (GHSV) was
10 adjusted to about 35,000. The temperature of the catalyst was increased from 150°C to 550°C and then reduced back to 150°C. Data were recorded as the temperature was reduced. In one evaluation, the Ag/alumina catalyst was placed upstream of the Cu/ZSM-5 catalyst. In the second and third evaluations, the catalysts were evaluated individually.

15

As shown in the graph of Figure 6, the results of the evaluations compare the performance of the combination of catalysts to the performances of the catalysts individually. Surprisingly, the performance of the combination of catalysts as represented by curve 46 was observed to be better than the additive performance of the
20 individual catalysts as represented by curves 48 and 50, respectively.

EXAMPLE 8

A set of ZSM-5 powders of varying crystal sizes and silica/alumina ratios were exposed to steam at a concentration of 10% water vapor for about 16 hours at 600°C to simulate aging induced by engine exhaust. The powders were subsequently pelleted and tested or evaluated for NO_x conversion. A second set of catalysts was prepared from same starting powders except the catalysts were impregnated with iron prior to being exposed to the steam. The second set of iron containing catalysts was prepared by adding 5.4 grams of iron (III) nitrate nonahydrate to 40 grams of deionized water under constant stirring. The resulting solution was added drop-wise to mix with 30 grams of ZSM-5. The impregnated powder was then dried overnight at about 85°C. The iron-containing ZSM-5 catalyst was air calcined at about 400°C for about 3 hours. The resulting catalysts contained 2.5 wt% iron.

The catalysts were evaluated using a quartz reactor heated in an electric furnace. A gas mixture containing 1000 ppm NO (nitric oxide), 1000 ppm propylene, 9% oxygen and the remaining portion being helium, was passed over the catalyst bed supported in the quartz reactor. The total flow rate of the gas mixture was about 1500 ml/min, and the catalyst volume was maintained at about 3.0 ml to yield a gas hourly space velocity (GHSV) of about 30,000. The temperature of the catalyst was increased from 150°C to 550°C and then reduced to 150°C. Data was recorded during the temperature reduction. The results are summarized in Table 1 below.

Table 1

Crystal size, μm	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Maximum NO_x conversion, %	
		H-ZSM-5	Fe-ZSM-5
0.02-0.05	60	8	10
0.5-2.0	50	14	17
0.5-2.0	25	8	10
5-8	80	8	8

- 5 The data shows that an optimized catalyst is generally obtained at an intermediate crystal size (0.5-2.0 μm) and intermediate $\text{SiO}_2/\text{Al}_2\text{O}_3$ (50). Although the metal in the metal-containing zeolite (ZSM-5) was iron, Applicants anticipate similar results for other related metals including copper.

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EXAMPLE 9

An evaluation was implemented which tested a combination catalyst consisting of Ag/alumina and Cu/ZSM-5 located downstream therefrom, and a combination catalyst consisting of Ag/alumina intermixed with Cu/ZSM-5. The catalysts were evaluated using a quartz reactor heated in an electric furnace. A gas mixture containing 1000 ppm NO (nitric oxide), 1000 ppm propylene, 2000 ppm hydrogen, 9% oxygen and the remaining portion being helium, was passed over the

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catalyst bed supported in the quartz reactor. The total flow rate of the gas mixture was about 1500 ml/min, and the catalyst volume was maintained at about 3.0 ml to yield a gas hourly space velocity (GHSV) of about 30,000. The temperature of the catalyst was increased from 150°C to 550°C and then reduced to 150°C. Data was recorded during the temperature reduction. The results are shown in Figure 7.

The results indicate that a mixed combination catalyst as represented by curve 52 operates less effectively than a staged catalyst having Ag/alumina upstream of Cu/ZSM-5 as represented by curve 54. The peak NO_x conversion to N₂ was about 63% for the staged catalyst while the mixed catalyst had a peak NO_x conversion to N₂ of about 43%.

EXAMPLE 10

A catalyst evaluation experiment was conducted in a quartz reactor heated in an electric furnace in accordance to the procedures described in Example 5 except the gas mixture passing over the catalyst bed included 7% water. The NO_x removing activity was measured at 475°C using the combination of Ag/alumina and downstream Cu/ZSM-5 catalysts with 3 wt% Cu loading, and the combination of Ag/alumina and downstream Pt/alumina with 1 wt% Pt loading. The results of the evaluation is shown in Figure 8. The combination of Ag/alumina and downstream Cu/ZSM-5 catalysts exhibited 80% NO_x conversion to N₂ as represented by bar 56, while the combination of Ag/alumina and downstream Pt/alumina exhibited 4% NO_x

conversion to N₂ as represented by bar 58.

Applicants believe that the initial reaction of NO_x with hydrocarbons on Ag/alumina catalysts results in the formation of intermediate species such as ammonia, amine,
5 organo-nitrogen species, and oxygenates. These intermediates desorb into the gas phase together with activated NO_x species. Further homogenous gas reaction leads to N₂ formation. These species are reacted on Cu/ZSM-5 for further reduction to N₂. However, the same species are reacted on Pt/alumina and oxidized to NO_x which drastically reduced NO_x conversion.

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Although various embodiments of the invention have been shown and described, they are not meant to be limiting. Those of skill in the art may recognize various modifications to these embodiments, which modifications are meant to be covered by the spirit and scope of the appended claims.

What is Claimed is:

1 1. An apparatus for catalytically processing a gas stream passing therethrough to
2 reduce the presence of NO_x therein, said apparatus comprising:

3 a first catalyst having a first optimal processing temperature range for catalytically
4 processing the gas stream; and

5 a second catalyst located downstream from the first catalyst, said second catalyst
6 having a second lower optimal processing temperature range relative to the first
7 temperature range for catalytically processing the gas stream subsequent to the first
8 catalyst.

1 2. The apparatus of claim 1, wherein the first and second catalysts are abutted
2 against one another.

1 3. The apparatus of claim 1, wherein the first and second catalysts are spaced apart
2 at a distance from one another.

1 4. The apparatus of claim 1, wherein the first and second catalysts are present in an
2 amount ratio ranging from about 1:2 to 2:1.

1 5. The apparatus of claim 1, wherein the first and second catalysts are present in an
2 amount ratio of about 1:1.

- 1 6. The apparatus of claim 1, wherein the gas stream further comprises a reductant.
- 1 7. The apparatus of claim 6, wherein the reductant is a hydrocarbon compound.
- 1 8. The apparatus of claim 1, wherein the first catalyst is metal-containing alumina.
- 1 9. The apparatus of claim 8, wherein the alumina is derived from a sol-gel synthesis
2 process.
- 1 10. The apparatus of claim 8, wherein the metal is selected from the group consisting
2 of silver, indium, gallium, tin and cobalt and mixtures thereof.
- 1 11. The apparatus of claim 8, wherein the metal is present in an amount of from
2 about 1 to 15 weight percent based on the total weight of the first catalyst.
- 1 12. The apparatus of claim 8, wherein the metal is present in an amount of from
2 about 2 to 5 weight percent based on the total weight of the first catalyst.
- 1 13. The apparatus of claim 1, wherein the first catalyst is silver-containing alumina.
- 1 14. The apparatus of claim 1, wherein the second catalyst is a metal-containing
2 zeolite.

1 15. The apparatus of claim 14, wherein the metal is selected from the group
2 consisting of copper, iron, cobalt, and silver and mixtures thereof.

1 16. The apparatus of claim 14, wherein the zeolite is selected from the group
2 consisting of ZSM-5, ZSM-11, ZSM-35, MCM-22, MCM-49, MCM-56, Beta, ITQ-13,
3 MCM-68.

1 17. The apparatus of claim 14, wherein the metal is present in an amount of from
2 about 2 to 15 weight percent based on the total weight of the second catalyst.

1 18. The apparatus of claim 14, wherein the metal is present in an amount of from
2 about 3 to 11.5 weight percent based on the total weight of the second catalyst.

1 19. The apparatus of claim 1, wherein the second catalyst is copper containing
2 zeolite.

1 20. The apparatus of claim 1, wherein the first and second catalysts are in the forms
2 selected from powders, pellets, monoliths, fluidized beds, and combinations thereof.

- 1 21. An apparatus for catalytically processing a gas stream passing therethrough
2 to reduce the presence of NO_x therein, said apparatus comprising:
3 a first catalyst comprising metal containing alumina, said first catalyst having a
4 first optimal processing temperature range for catalytically processing the gas stream;
5 and
6 a second catalyst comprising metal containing zeolite located downstream from
7 the first catalyst, said second catalyst having a second lower optimal processing
8 temperature range relative to the first optimal processing temperature range for
9 catalytically processing the gas stream subsequent to the first catalyst.
- 1 22. The apparatus of claim 21, wherein the first and second catalysts are abutted
2 against one another.
- 1 23. The apparatus of claim 21, wherein the first and second catalysts are spaced
2 apart at a distance from one another.
- 1 24. The apparatus of claim 21, wherein the first and second catalysts are present in
2 an amount ratio ranging from about 1:2 to 2:1.
- 1 25. The apparatus of claim 21, wherein the first and second catalysts are present in
2 an amount ratio of about 1:1.
- 1 26. The apparatus of claim 21, wherein the gas stream further comprises a reductant.

1 27. The apparatus of claim 25, wherein the reductant is a hydrocarbon compound.

1 28. The apparatus of claim 21, wherein the metal is selected from the group
2 consisting of silver, indium, gallium, tin and cobalt and mixtures thereof.

1 29. The apparatus of claim 21, wherein the metal is present in an amount of from
2 about 1 to 15 weight percent based on the total weight of the first catalyst.

1 30. The apparatus of claim 21, wherein the metal is present in an amount of from
2 about 2 to 5 weight percent based on the total weight of the first catalyst.

1 31. The apparatus of claim 21, wherein the alumina is derived from a sol gel
2 synthesis process.

1 32. The apparatus of claim 21, wherein the first catalyst is silver containing alumina.

1 33. The apparatus of claim 21, wherein the metal is selected from the group
2 consisting of copper, iron, cobalt, and silver and mixtures thereof.

1 34. The apparatus of claim 21, wherein the zeolite is selected from the group
2 consisting of ZSM-5, MCM-22, MCM-49, MCM-56, Beta, ITQ-13, MCM-68, ZSM-35 and
3 ZSM-11.

1 35. The apparatus of claim 21, wherein the metal is present in an amount of from
2 about 2 to 15 weight percent based on the total weight of the second catalyst.

1 36. The apparatus of claim 21, wherein the metal is present in an amount of from
2 about 3 to 11.5 weight percent based on the total weight of the second catalyst.

1 37. The apparatus of claim 21, wherein the second catalyst is copper containing
2 zeolite.

1 38. The apparatus of claim 21, wherein the first and second catalysts are in the forms
2 selected from powders, pellets, monoliths, fluidized beds, and combinations thereof.

1 39. A method for making an apparatus for catalytically processing a gas stream
2 passing therethrough to reduce the presence of NO_x therein, said method comprising
3 the steps of:

4 acquiring a first catalyst being adapted for catalytically processing the gas stream
5 at a first temperature range; and

6 positioning a second catalyst downstream from the first catalyst, wherein said
7 second catalyst is adapted for catalytically processing the gas stream at a lower second
8 temperature range relative to the first temperature range.

1 40. The method of claim 39, further including the step of spacing apart said first and

2 second catalysts.

1 41. A method for catalytically processing a gas stream to reduce the presence of NO_x
2 therein, said method comprising the steps of:

3 delivering the gas stream to a first catalyst having a first optimal processing
4 temperature range for catalytically processing the gas stream; and

5 conveying the gas stream from the first catalyst to a second catalyst wherein said
6 second catalyst has a lower second optimal processing temperature range relative to
7 the first optimal processing temperature range for catalytically processing the gas
8 stream subsequent to the first catalyst.

1 42. The method of claim 41, prior to delivery of the gas stream to the first catalyst,
2 further comprising the step of injecting into the gas stream a reductant in an amount
3 sufficient to facilitate the reduction of NO_x in the gas stream.

1 43. The method of claim 41, further including the step of spacing apart said first and
2 second catalysts.

1 44. The method of claim 42, further including the step of spacing apart said first and
2 second catalysts.

1 45. An apparatus for catalytically processing a gas stream passing therethrough
2 to reduce the presence of NO_x therein, said apparatus comprising:
3 a first catalyst adapted for facilitating the reaction of NO_x with hydrocarbons to
4 yield intermediates in the form of nitrogen containing compounds and activated NO_x;
5 and
6 a second catalyst located downstream from the first catalyst, said second
7 catalyst adapted for facilitating the reactions of the intermediates into N₂ subsequent
8 to the first catalyst.

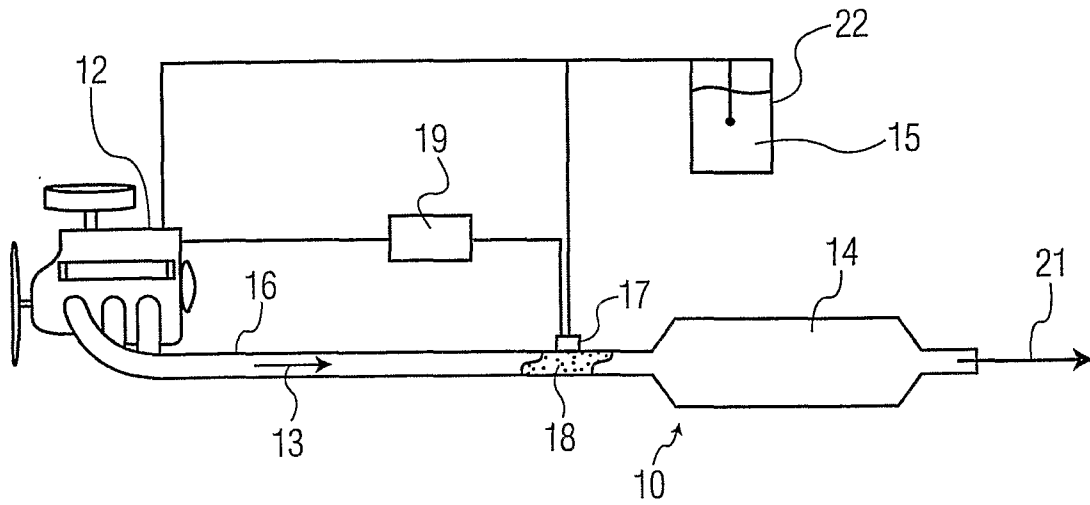


FIG. 1

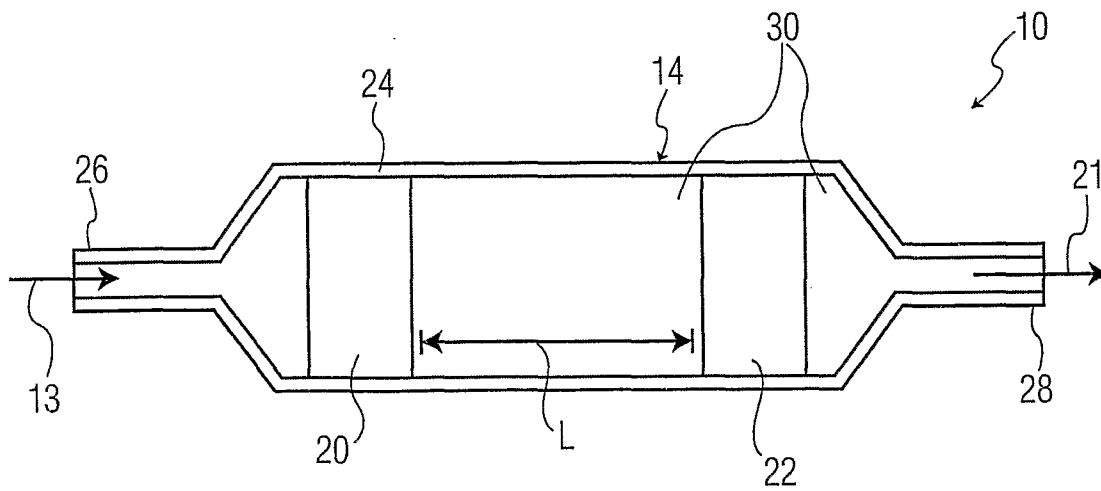


FIG. 2

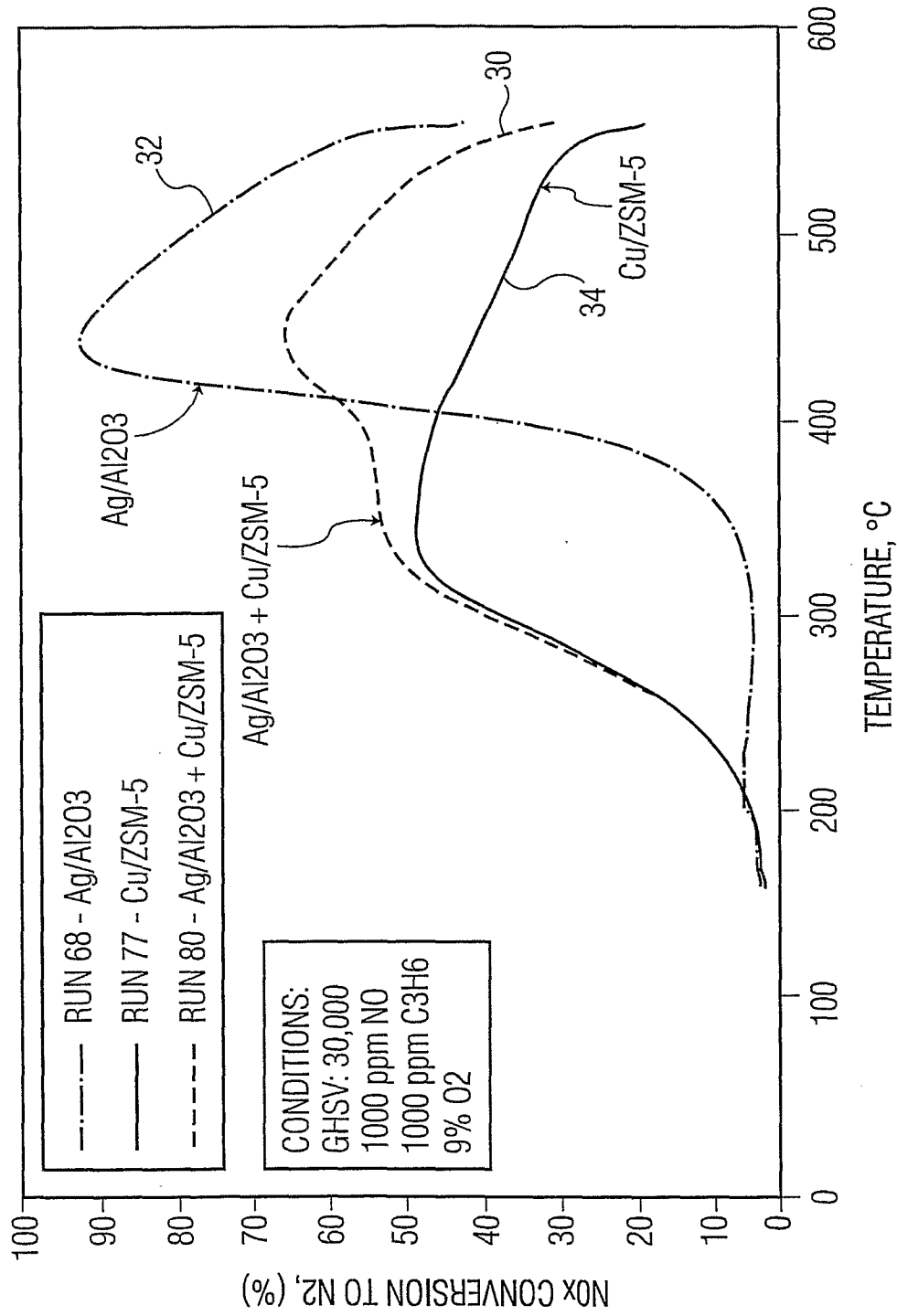


FIG. 3

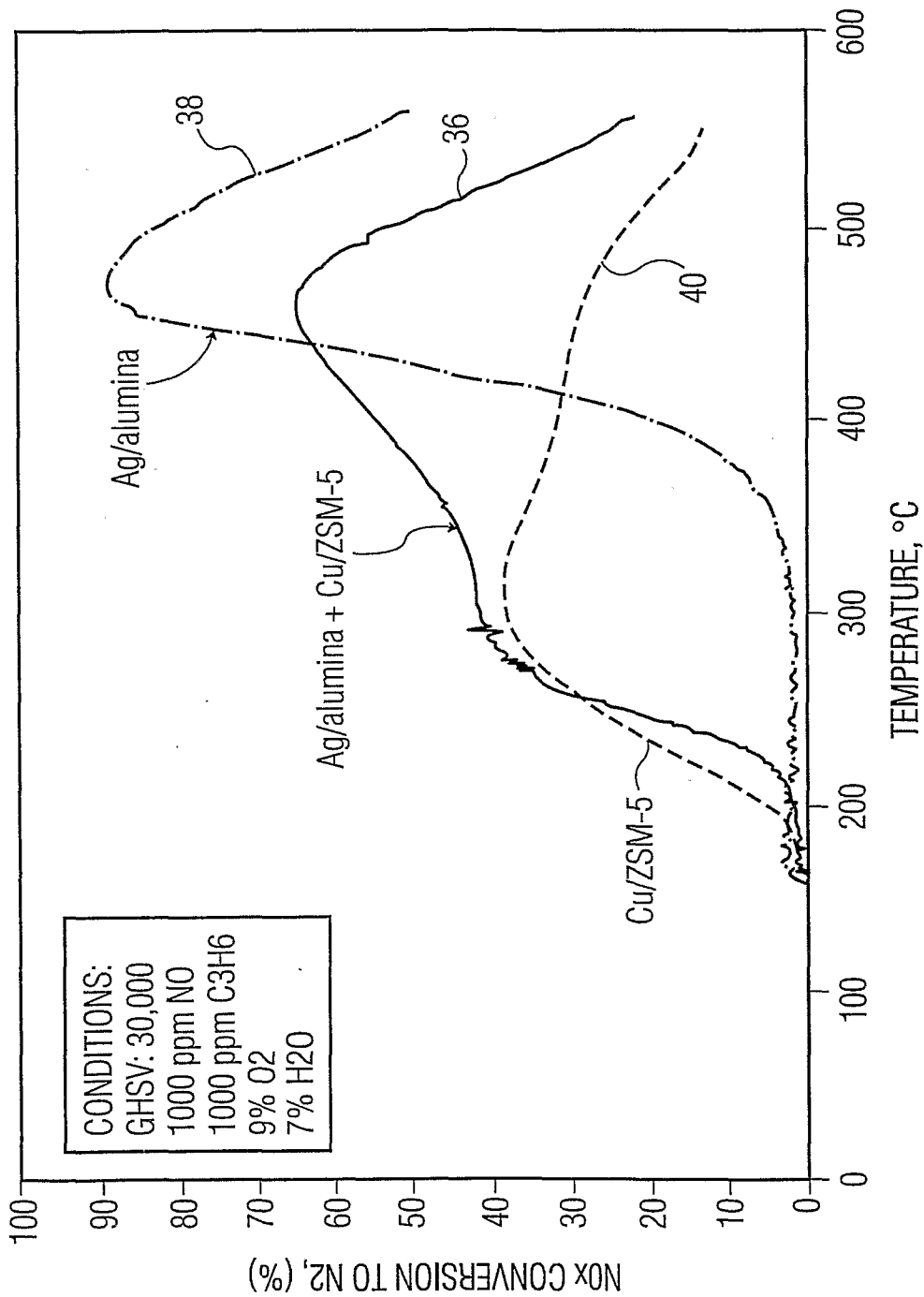


FIG. 4

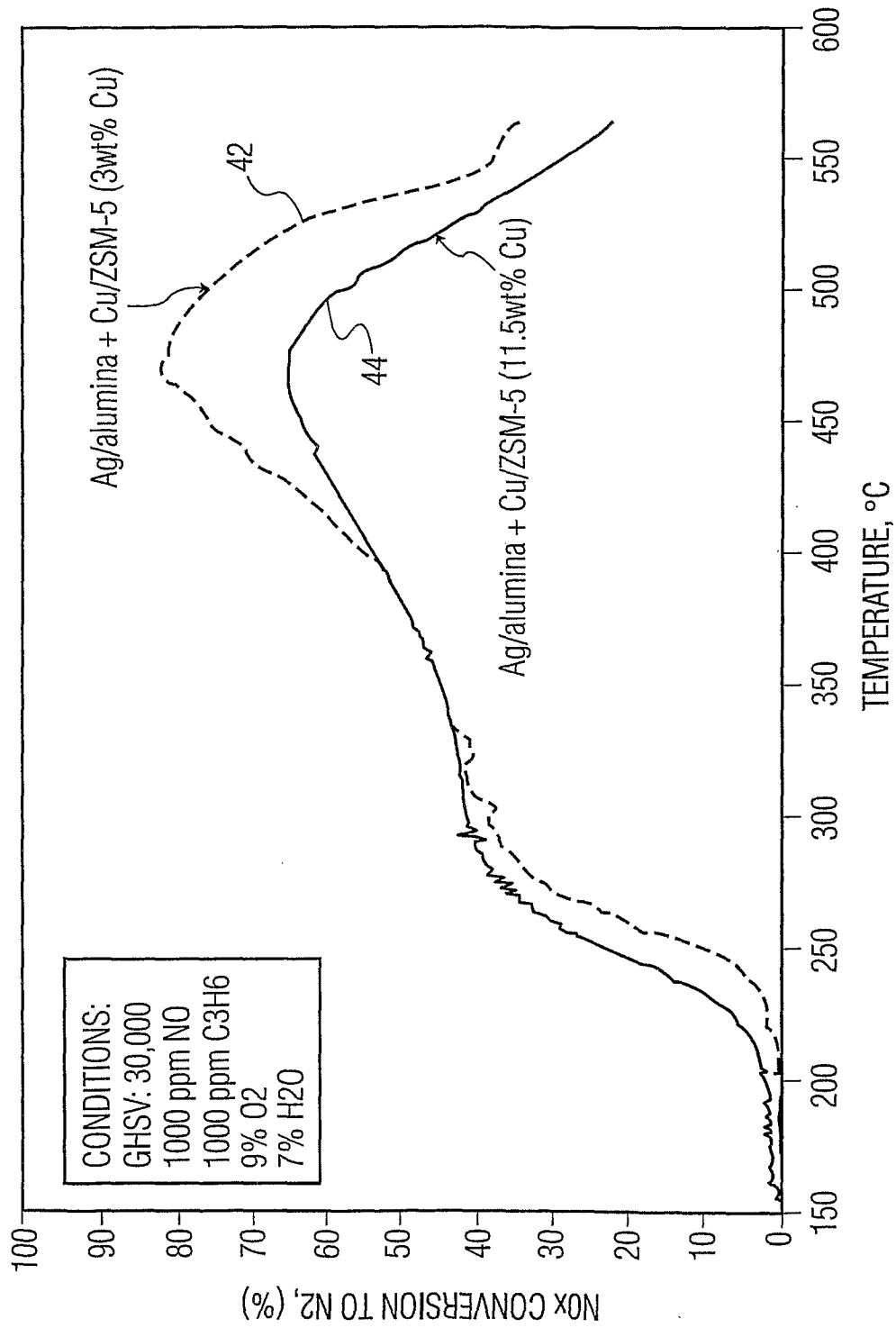


FIG. 5

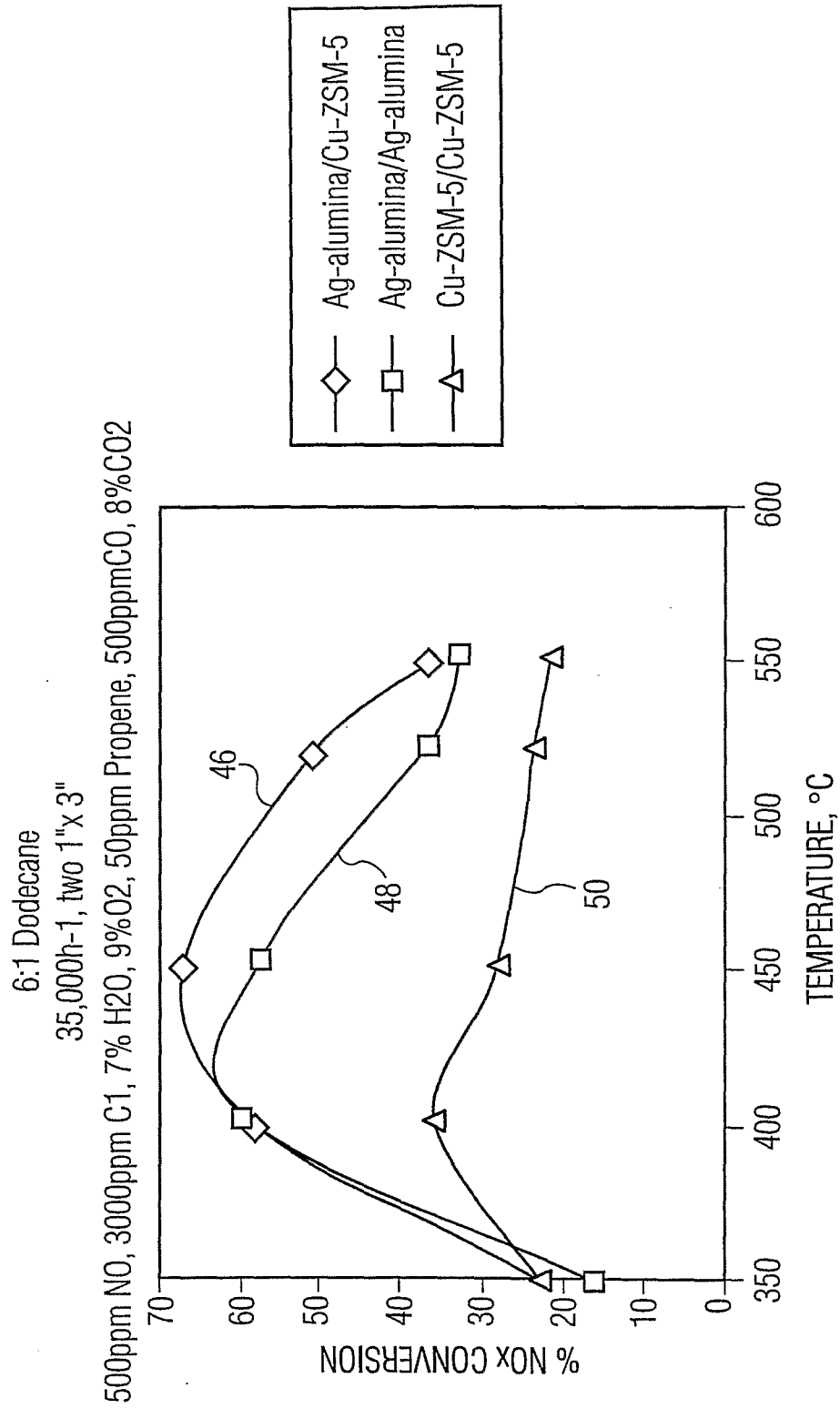


FIG. 6

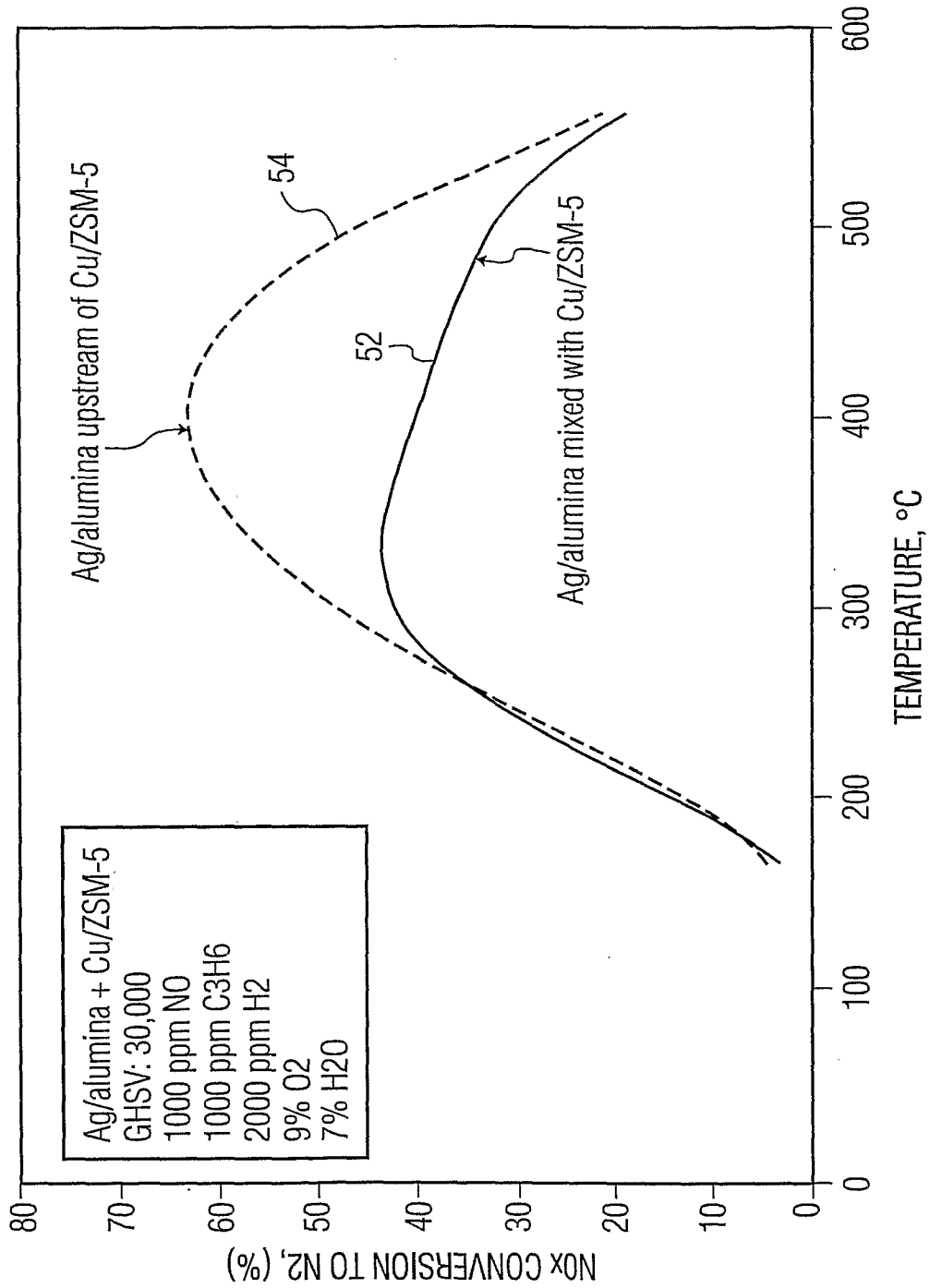


FIG. 7

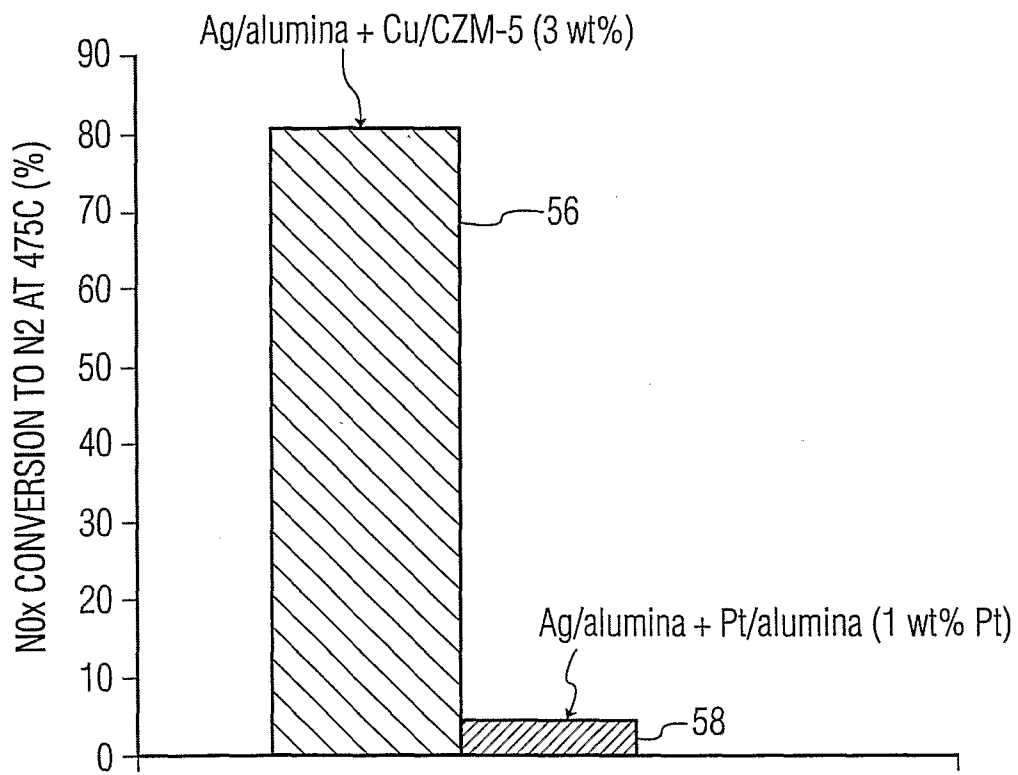


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/005464

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/94 B01J23/50 B01J29/46

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)
B01D B01J

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, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2005/016496 A (JOHNSON MATTHEY PUBLIC LIMITED COMPANY; STANISLAW, EDMUND, GOLUNSKI; H) 24 February 2005 (2005-02-24) page 4, line 5 - line 27 page 8, line 14 - line 31 page 10, line 6 - page 11, line 10; claims; figure 10 ----- -/--	1-45

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p>
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Date of the actual completion of the international search <p style="text-align: center;">29 June 2006</p>	Date of mailing of the international search report <p style="text-align: center;">10/07/2006</p>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center;">Eijkenboom, A</p>
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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/005464

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X	WO 00/64566 A (VOLKSWAGEN AKTIENGESELLSCHAFT; POTT, EKKEHARD) 2 November 2000 (2000-11-02) page 3, paragraph 4 - page 4, paragraph 1 page 5, paragraph 1 page 6, paragraph 3 - page 8, paragraph 1; figure 1 -----	1, 3-9, 11, 12, 20, 39-44
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A	US 6 314 722 B1 (MATROS YURII SH ET AL) 13 November 2001 (2001-11-13) column 4, line 47 - column 5, line 4 -----	1-45

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Information on patent family members

International application No

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