Title: CALCINATION MODULE FOR A COATING PROCESS

**Abstract:** A method for on-line calcination of a dried coating medium or washcoat located within the channels of monolithic substrates is provided. The method relies on the forcing of a stream of heated gas through the substrate at a temperature of at least about 400 °C. Further provided is a modular calcination apparatus for calcining a dried coating medium on a monolithic substrate having the dried coating medium within a plurality of channels in the substrate. The modular apparatus includes means for transporting a dried coated monolithic substrate from a drying station to a housing; gasket means for sealing the dried coated monolithic substrate in the housing; heating means for providing a heated gas in the housing at a temperature of at least about 400 °C; forced gas stream means for forcing the heated gas through the dried coated monolithic substrate to produce a dried and calcined coating on the monolithic substrate; and means for removing the calcined coated monolithic substrate.
CALCINATION MODULE FOR A COATING PROCESS

TECHNICAL FIELD OF THE INVENTION

Principles and embodiments of the present invention relate generally to systems and methods of calcining a catalytic substrate as part of a continuous catalytic coating operation.

BACKGROUND OF THE INVENTION

Catalytic converters are well known for the removal and/or conversion of the harmful components of exhaust gases. While catalytic converters have a variety of constructions for this purpose, one form of construction is a catalytically coated rigid skeletal monolithic substrate or honeycomb-type element which has a multiplicity of longitudinal channels to provide a catalytically coated body having a high surface area. The rigid, monolithic substrate is fabricated from ceramics and other materials. Such materials and their construction are described, for example, in U.S. Pat. Nos. 3,331,787 and 3,565,830, each of which is incorporated herein by reference.

A monolithic honeycomb substrate typically has an inlet end and an outlet end, with multiple mutually adjoining cells extending along the length of the body from the inlet end to the outlet end. These honeycomb substrates typically have from about 100 to 600 cells-per-square-inch (cpsi), but may have densities range from 10 cpsi to 1200 cpsi. Cells having round, square, triangular, or hexagonal cell shapes are known in the art. The open frontal area may comprise 50% to 85% of the surface area, and the cell wall thickness may be from 0.5 to 10 mils, where 1 mil is 0.001 inches. The cells also may be separated from one another by walls with a thickness in the range of about 0.5 mil to about 60 mils (0.012 mm to 1.5 mm). In some cases, the open frontal area may be as much as 91% for a 600 cpsi substrate with 2 mil cell wall thickness. The cell walls of the substrate may be porous or non-porous, smooth or rough. For porous walls, an average wall pore diameter may be from about 0.1 to about 100 microns, and wall porosity may typically range between about 10-85%.

The monolithic substrate and particularly the multiplicity of channels are coated with a slurry of a catalytic and/or absorbent material (hereinafter referred to collectively as a "coating medium"), which may comprise the catalytic and/or absorbent material in solution form or in suspended form. The slurry contains water and possibly other liquid constituents which upon heating are vaporized. Monolithic substrates may have one, two, or more such catalytic and/or absorbent material-containing coating media deposited thereon. While various methods are known in the art for coating a monolithic substrate with a coating medium, such methods from the standpoint of cost are deficient in minimizing the amount of coating medium applied, especially when a costly catalytically active precious metal such as platinum, palladium or rhodium is deposited as part of the coating medium. Not only can it be difficult to coat monolithic substrates, but it can also be difficult to provide a consistent and reproducible coating pattern within the channels.

One method of coating a prefabricated monolithic substrate is to pump the coating media into the respective channels and then subject the coated substrate to a drying operation. Drying is a necessary step in
the coating process so as to remove vaporized constituents (e.g. water vapor) and rapidly fix the coating medium in the channels. Systems which employ a drying operation may be unsuccessful in providing a uniform coating thickness and a uniform coating profile wherein the coating media is deposited uniformly over the same length of each of the channels.

High temperature catalysts, e.g. three way catalysts (TWC), have utility in a number of fields including the abatement of nitrogen oxide (NOx), carbon monoxide (CO) and hydrocarbon (HC), such as non-methane hydrocarbon (NMHC), pollutants from internal combustion engines, such as automobile and other gasoline-fueled engines. Three-way conversion catalysts are poly-functional because they have the ability to substantially and simultaneously catalyze the oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides. Emissions standards for nitrogen oxides, carbon monoxide, and unburned hydrocarbon contaminants have been set by various government agencies and must be met by new automobiles. In order to meet such standards, catalytic converters containing a TWC catalyst are located in the exhaust gas line of internal combustion engines.

TWC catalysts exhibiting good activity and long life comprise one or more platinum group metals, e.g., platinum, palladium, rhodium, ruthenium, and iridium. These catalysts are employed with a high surface area refractory oxide support. The refractory metal oxide can be derived from aluminum, titanium, silicon, zirconium, and cerium compounds, resulting in the oxides with the exemplary refractory oxides including at least one of alumina, titania, silica, zirconia, and ceria. Generally, the TWC catalysts are supported by gamma-alumina. The TWC catalytic support is carried on a suitable carrier or substrate such as a monolithic carrier comprising a refractory ceramic or metal honeycomb structure, or refractory particles such as spheres or short, extruded segments of a suitable refractory material.

As emphasized above, high surface refractory metal oxides are often employed as a support for many of the catalytic components. For example, high surface area alumina materials, also referred to as "gamma alumina" or "activated alumina", used with TWC catalysts typically exhibit a BET (Brunauer, Emmett, and Teller) surface area in excess of 60 m²/g, and often up to about 200 m²/g or more. Such activated alumina is usually a mixture of the gamma and delta phases of alumina, but may also contain substantial amounts of eta, kappa, and theta alumina phases. Refractory metal oxides other than activated alumina may be utilized as a support for at least some of the catalytic components in a given catalyst. For example, bulk ceria, zirconia, alpha-alumina and other materials are known for such use. Although many of these materials have a lower BET surface area than activated alumina, that disadvantage tends to be offset by the greater durability of the resulting catalyst.

Exhaust gas temperatures can reach 1000°C in a moving vehicle employing a catalytic converter, and such elevated temperatures can cause activated alumina, or other support material, to undergo thermal degradation with accompanying volume shrinkage in the presence of steam. During this degradation, the catalytic metal becomes sintered on the shrunken support medium with a loss of exposed catalyst surface area and a corresponding decrease in catalytic activity.

In order to prevent sintering of catalytic metals, the unstable support is doped with a stabilizing material similar to the process described above. The stabilization of TWC catalysts is known in the art. For
example, U.S. Pat. No. 4,171,288 discloses a method to stabilize alumina supports against such thermal degradation by the use of doping materials such as zirconia, titania, alkaline earth metal oxides of barium, calcium, or strontium, or rare earth metal oxides such as ceria, lanthana, and mixtures of two or more rare earth metal oxides.

Preparation of alumina-supported catalysts typically can involve two production steps: drying at a temperature of 100°C followed by calcining at an excess of 500°C over many hours. One problem encountered in production of supported catalysts is in the calcination of the catalyst coating layers. Appropriate high temperatures can be required to fully decompose coating media ("washcoats") depositing the catalyst materials, and to prevent migration of components resulting in disadvantageous doping of precious metals within the catalyst.

In the past, calcination has been performed off-line after drying of a washcoat. See, for example, U.S. Patent 5,953,832 for a representative drying procedure, herein incorporated by reference. However, the process can take an hour or more to complete, and problems have been encountered in off-line calcination using conveyor belt ovens. Air flow through heating zones is minimal, making conductive heating the primary mechanism for decomposition, namely calcination, of the washcoat. Uneven heating of substrate pieces, and consequent thermal stress to those pieces resulted. A radial temperature gradient has been observed across pieces coated in this manner, indicating both longitudinal and radial stress which are most evident upon cool down. Furthermore, based on these observations it was believed that increased temperatures, which would be needed to perform more rapid on-line calcination, would result in thermal shock leading to cracking of substrates.

It would be desirable to develop further methods for calcining monolithic catalytic substrates and, in particular, methods for calcination on-line at higher temperatures in a more uniform manner than that observed using an off-line conduction oven, to provide improved production line efficiency, speed, energy and cost savings.

**SUMMARY OF THE INVENTION**

Various embodiments are listed below. It will be understood that the embodiments listed below may be combined not only as listed below, but in other suitable combinations in accordance with the scope of the invention.

In one embodiment, an on-line method is provided for calcining a dried coating medium or washcoat located within the channels of monolithic substrates which have been coated with a coating medium or washcoat. The method provides for calcination in a rapid manner while maintaining a uniform coating profile. The term "uniform coating profile" as used herein means that each channel of the substrate will be coated over approximately the same length, typically less than the entire length of the substrate. Exhaust gas purification catalysts coated on such substrates are contemplated, which are useful in emission treatment or control systems.

The method relies on the forcing of a stream of gas (at an elevated temperature) through the substrate to carry out the decomposition process in the coating. As such, in some aspects, the present
invention generally relates to a method of calcining a monolithic catalytic substrate having a washcoat layer by forcing hot air into an end of the monolithic catalytic substrate to remove liquid material while affixing the slurry and catalytic material onto the surface of the interior walls of the catalytic substrate.

In particular, certain aspects are directed to an on-line method of calcining a dried coating medium on a monolithic substrate having the dried coating medium within a plurality of channels in the substrate, comprising the steps of:

(a) transporting a dried coated monolithic substrate from a drying station to a housing;
(b) providing a heated gas stream within the housing at a temperature of at least about 400 °C; and
(c) forcing the heated gas stream through the plurality of channels of the dried coated monolithic substrate to produce a dried and calcined coating on the monolithic substrate. The calcination step can be carried out in about 5 seconds to about 25 seconds on a production line. In a further embodiment the calcination step can be carried out in about 10 seconds to about 15 seconds on a production line.

In another embodiment, a modular apparatus is provided for calcining a dried coating medium on a monolithic substrate having the dried coating medium within a plurality of channels in the substrate. The modular apparatus includes: means for transporting a dried coated monolithic substrate from a drying station to a housing; gasket means for sealing the dried coated monolithic substrate into the housing; heating means for providing a heated gas in the housing at a temperature of at least about 400 °C; forced gas stream means for forcing the heated gas through the dried coated monolithic substrate to produce a dried and calcined coating on the monolithic substrate; and means for removing the calcined coated monolithic substrate.

In further specific embodiments, the present disclosure provides an apparatus for calcining a monolithic catalytic substrate comprising: a substrate-receiving portion comprising an upper calciner section and a lower calciner section, wherein the upper calciner section and the lower calciner section are configured and dimensioned to fit over a catalytic substrate and form a fluid-tight seal when in a closed position; and a heating fluid source, which provides a heating fluid at an intended temperature, operatively associated and in fluid communication with the lower calciner section, wherein the heating fluid is delivered to an inlet end of the lower calciner section.

In certain embodiments, the apparatus further comprises a heating fluid pump operatively associated and in fluid communication with the heating fluid source to propel the heating fluid through the heating fluid source where the temperature of the heating fluid is increased to an intended temperature. In certain embodiments, the heating fluid is a gas and the heating fluid pump is a blower or compressor that produces a heating fluid volumetric flow rate in the range of about 50 scfm to about 150 scfm. In some embodiments, the heating fluid source is a hot air combustion system comprising a combustion chamber and a gas burner that increases the temperature of the heating fluid to the intended temperature in the range of about 350°C to about 550°C. In further embodiments, the heating fluid source is a heat exchanger that increases the temperature of the heating fluid to the intended temperature in the range of about 350°C to about 550°C.

The apparatus can further comprise various other components and stations. For example, in some embodiments, the apparatus further comprises a transfer duct operatively associated and in fluid
communication with the heating fluid source and the lower calciner section, wherein the transfer duct forms a fluid path between the heating fluid source and the lower calciner section; a water reservoir for providing a quantity of deionized water for injection into the entry duct; an injection nozzle projecting into the entry duct; and a water pump operatively associated with the water reservoir and the injection nozzle that propels the water from the reservoir through the injection nozzle into the entry duct for de-greening a catalytic substrate. In some embodiments, such an apparatus further comprises a safety interlock comprising a water pump controller and a temperature sensor operatively associated with the source duct, wherein the interlock prevents the water pump from operating and shuts the water pump off if the temperature of the entry duct detected by the temperature sensor is below the intended operating temperature. In certain embodiments (e.g., wherein a heating fluid comprising a gas is employed), the apparatus can further comprise an exhaust duct operatively associated and in fluid communication with the upper calciner section to evacuate the heating fluid.

The apparatus, in some embodiments, further comprises a by-pass duct connected to and in fluid communication with the source duct; a bypass control valve inserted into and operatively associated with the by-pass duct; and a calcining control valve inserted into and operatively associated with the source duct down-stream of the by-pass duct, wherein the calcining control valve and the bypass control valve function in tandem to redirect the heating fluid from the lower calciner section to the by-pass duct. Such an apparatus can, in certain embodiments, further comprise an inlet pressure transducer operatively associated with the lower calciner section, which generates an inlet pressure value of the heating fluid entering the lower calciner section; an outlet pressure transducer operatively associated with the upper calciner section, which generates an outlet pressure value of the heating fluid exiting the upper calciner section; and a differential pressure controller in electrical communication with the inlet pressure transducer and outlet pressure transducer that calculates the pressure difference between the outlet pressure value and the inlet pressure value, and adjusts the heating fluid pump to propel more or less heating fluid through the heating fluid source depending on the pressure difference. In certain embodiments, the heating fluid is diverted to the exhaust duct by closing the calcining control valve and opening the bypass valve in tandem when the upper calciner section and the lower calciner section are not in a closed position.

In another aspect, a method of calcining a catalytic substrate is provided, the method comprising positioning a catalytic substrate comprising a plurality of longitudinal cells between a lower calciner section and an upper calciner section; moving the upper calciner section and/or lower calciner section linearly to encase the catalytic substrate within the upper calciner section and lower calciner section, wherein a fluid-tight seal is formed by the upper calciner section and the lower calciner section around the catalytic substrate such that a heating fluid delivered to an inlet end of the lower calciner section passes through the plurality of longitudinal cells of the catalytic substrate; and delivering a heating fluid at an intended temperature to an inlet end of the lower calciner section. The heating fluid, in some embodiments, is delivered to the inlet end of the lower calciner section at a volumetric flow rate in the range of about 50 scfm to about 150 scfm.

In some embodiments, the method further comprises propelling the heating fluid with a heating fluid pump at an intended volumetric flow rate to a heating fluid source operatively associated with the heating
fluid pump; and heating the heating fluid up to an intended temperature within the heating fluid source prior to delivering the heating fluid at the intended temperature to an inlet end of the lower calciner section. For example, in some embodiments, the heating fluid is heated to the intended temperature in the range of about 350°C to about 550°C. The method, in certain embodiments, can further comprise conveying the heating fluid from the heating fluid source to the inlet end of the lower calciner section through a delivery duct; and injecting a spray of water into the delivery duct if the heating fluid being conveyed through the transfer duct is at the intended temperature. The intended temperature of the heating fluid being conveyed through the transfer duct, in some embodiments, is in the range of about 450°C to about 550°C.

A method of manufacturing a plurality of catalytic substrates is also provided herein, comprising transferring each of the plurality of catalytic substrates from a preceding station to a subsequent station in a sequential manner, where each station preforms a production operation including at least coating, drying, and calcining on the catalytic substrates.

In a further aspect, the disclosure provides a system for preparing a catalytic substrate (which may be referred to herein as a "multi-station catalytic substrate processing system"), generally comprising one or more coating apparatus, one or more calcining apparatus, one or more weighing apparatus, one or more drying apparatus, one or more transfer apparatus, and/or a loading apparatus, where the calcining apparatus receives a catalytic substrate with a wet washcoat layer from a preceding station in the multi-station catalytic substrate processing system.

More particularly, the disclosure provides a system for preparing a catalytic substrate comprising: a first catalytic substrate coating station that applies at least one washcoat comprising a catalytic slurry and a liquid carrier to at least a portion of the catalytic substrate; at least one drying station that removes at least a portion of the liquid carries from the at least a portion of the catalytic substrate; and one or more calcining stations comprising an upper calciner section and a lower calciner section, wherein the upper calciner section and the lower calciner section are configured and dimensioned to fit over the catalytic substrate and form a fluid-tight seal, and a heating fluid source that supplies a volume of heating fluid at an intended temperature operatively associated with the lower calciner section, wherein the heating fluid is delivered to an inlet end of the lower calciner section to calcine the catalytic slurry of the washcoat to the cell walls of the catalytic substrate; and a substrate gripper that holds the catalytic substrate and transfers the catalytic substrate between the catalytic substrate coating station, the at least one drying station, and the one or more calcining stations, wherein one calcining station of the one or more calcining stations is adjacent to one of the at least one drying stations.

In certain embodiments, the substrate gripper comprises a silicone rubber insert that can operate continuously at 600°F. In some embodiments, the system further comprises a second catalytic substrate coating station that applies at least one additional washcoat comprising a catalytic slurry and a liquid carrier to at least a portion of the catalytic substrate after the catalytic substrate has been calcined at least once at the one or more calcining station; and at least one weighing station that measures the weight of the catalytic substrate, wherein the substrate gripper transfers the catalytic substrate from the catalytic substrate coating
station, the drying station, or the calcining station to the at least one weighing station to determine a wet and/or a dry weight of the catalytic substrate.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 illustrates an exemplary embodiment of an inline calcining apparatus depicting a substrate-receiving portion in an open position;

FIG. 2 illustrates an exemplary embodiment of an inline calcining apparatus depicting a substrate-receiving portion in a closed position;

FIG. 3 illustrates an exemplary embodiment of a an inline calcining apparatus depicting a substrate-receiving portion in a closed position against a substrate gripper;

FIG. 4 illustrates another exemplary embodiment of an inline calcining apparatus depicting a substrate-receiving portion in a closed position;

FIG. 5A illustrates a detailed view of an exemplary embodiment of an upper calciner section and lower calciner section of a substrate-receiving portion;

FIG. 5B illustrates a cross-section of an exemplary embodiment of an upper calciner section of a circular substrate-receiving portion;

FIG. 5C illustrates a cross-section of an exemplary embodiment of an upper calciner section of a rectangular substrate-receiving portion;

FIG. 5D illustrates a cross-section of an exemplary embodiment of a lower calciner section of a circular substrate-receiving portion;

FIG. 5D illustrates a cross-section of an exemplary embodiment of a lower calciner section of a rectangular substrate-receiving portion;

FIG. 6A illustrates a top view of an exemplary embodiment of a gripper assembly for holding a catalytic substrate;

FIG. 6B illustrates a front cut-away view of an exemplary embodiment of a gripper assembly for holding a catalytic substrate;

FIG. 7 illustrates an exemplary embodiment of a method of calcining a catalytic substrate;

FIG. 8 illustrates an exemplary embodiment of a method of calcining a catalytic substrate.

FIG. 9A depicts a density plot indicating that calcination on-line improves thermal shock parameter;

FIG. 9B depicts a failure frequency plot indicating that calcination on-line improves thermal shock parameter;

FIG. 10 depicts a graph of heat transfer (time vs. temperature) at various locations in an embodiment of the modular calcination apparatus;

FIG. 11A depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and Rh (top coat) in a control double-coat control catalyst sample;

FIG. 11B depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and La, Ba, and Sr (top coat) in a control double-coat control catalyst sample;
FIG. 12A depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and Rh (top coat) in a double-coat catalyst sample prepared using on-line calcination at 400°F/200°C;

FIG. 12B depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and La, Ba, and Sr (top coat) in a double-coat catalyst sample prepared using on-line calcination at 400°F/200°C;

FIG. 13A depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and Rh (top coat) in a double-coat catalyst sample prepared using on-line calcination at 575°F/300°C;

FIG. 13B depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and La, Ba, and Sr (top coat) in a double-coat catalyst sample prepared using on-line calcination at 575°F/300°C;

FIG. 14A depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and Rh (top coat) in a double-coat catalyst sample prepared using on-line calcination at 750°F/400°C;

FIG. 14B depicts Electron Probe Micro Analysis (EPMA) of Pd (bottom coat) and La, Ba, and Sr (top coat) in a double-coat catalyst sample prepared using on-line calcination at 750°F/400°C;

FIG. 15 depicts engine data obtained according to standard protocols using catalysts of Examples 3, 4, and 5 prepared using on-line calcination relative to a control catalyst;

FIG. 16A depicts a SEM photomicrograph of a cross-sectional view of a double coat control catalyst sample on a support; and

FIG. 16B depicts a SEM photomicrograph of a cross-sectional view of a double coat catalyst sample prepared using on-line calcination at 750°F/400°C as in Experiment No. 8 of Example 5 on a support.

DETAILED DESCRIPTION OF THE INVENTION

It is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

In one aspect, a method of calcination is provided such that a substrate or work piece can be processed (e.g., coated) and calcined on-line by addition of a calcination module to existing equipment.

Exemplary coating systems embodied in such existing equipment are described in U.S. Patent Nos. 7,374,792 and 5,866,210, herein incorporated by reference in their entireties. These known systems are generally known as single pass double coat (SPDC) and single pass double coat combo (SPDC²) systems.

Current off-line production calciners operate on a principle of conduction-creating temperature gradients, which can lead to product failure due to thermal shock, especially at temperatures in excess of 400°C. In one embodiment of the present disclosure, a modular calcination apparatus operating on a principle of convection is provided that can operate on-line at temperatures of at least about 400°C, while reducing thermal shock failure to acceptable levels.

Incorporating an additional component (i.e., an in-line calciner) into existing coating systems will increase the instantaneous cycle time per station for processing a catalyst. The standard process coats one half of the substrate in 9-11 seconds on one side of the machine and then coats the other half of the substrate on the other side of the machine. Subsequently, the full single-layer coat is conveyed to a belt calciner, where it is
calcined and the next coating layer must be applied be reloading the coated substrate back into the machine for a second application.

According to one process of the present disclosure, installation of a calcination module as disclosed herein in order to coat and calcine a substrate by applying wet/wet coating process logic, will require a flip of the substrate between half coats, which will increase the instantaneous cycle time from 9 seconds to roughly 16 seconds per station. However, during these 16 seconds, two coats are applied instead of one (namely, one full coat on the front side of the machine and a second full coat applied on the back side of the machine), which actually reduces substrate handling and the overall cycle time to produce a double layer catalyst by ca. 10%.

While combination coating methods such as that described in U.S. Patent No. 7,374,792, using the installed calcination module will increase the instantaneous cycle time per station from 9 to 11 seconds, these methods also double the number of coats applied, reducing the overall cycle time to produce a double layered catalyst by ca. 40%. As such, in some embodiments, methods of increasing the rate a catalytic precursor is prepared are provided, by eliminating off-line calcining of the catalytic material adsorbed onto the cell walls of the catalytic substrate.

Certain aspects of the present invention relates generally to a coating system for preparing a catalytic substrate. The coating system may comprise a first catalytic substrate coating station that applies at least one washcoat comprising a catalytic slurry and a liquid carrier to at least a portion of the catalytic substrate, at least one drying station that removes at least a portion of the liquid carries from the at least a portion of the catalytic substrate, and one or more inline calcining stations, also referred to as an inline calciner.

Various principles and embodiments of the present invention relate to a calcining system that holds a catalytic substrate within an enclosed chamber, and utilizes a heating fluid to heat the interior of a catalytic substrate up to a calcining temperature. Using the presently disclosed calcination module in-line with an existing system, the present process can optionally incorporate off-line calcination in at least one of the steps, or eliminate off-line calcination altogether, thus maximizing production efficiency. However, full calcination module integration is contemplated on both sides of such coating machines, which will produce a standalone coater capable of double coating, drying, and calcination. The observed increases in cycle time efficiency represent an unexpected and statistically significant improvement over the state of the art. Also, as discussed above, in-line installation of a calcination module as disclosed herein is expected to improve overall coater efficiency by about 10% to 40%, thus improving production capacity.

In general, a preformed monolithic substrate, which can be made of ceramic or metals or other suitable material (as described further herein below) can be coated with a coating medium such as a catalytic composition, an absorbent composition or both. The coating medium can be in the form of a slurry containing constituents (e.g. water) which vaporize during the coating operation. The slurry can be applied to the monolithic substrate by various coating methods, for example, dipping, spraying or vacuum infusion (imposing a vacuum on one end of the substrate to thereby draw the coating media upwardly from a vessel, as disclosed in U.S. Patent No. 5,953,832, which is incorporated herein by reference).
Conventional drying of coated substrates employs evaporation alone or evaporation in conjunction with the blowing of hot air from the bottom end of the substrate through the top end. The blowing of hot air imposes pressure on the vapor and causes it to rise out of the channels. However, the amount of water vapor present in the channels and the pressure gradient made thereby can require a significant force to blow the vapor out of the channels. The use of excessive force can have an adverse impact on the coating medium and particularly the coating profile. In particular, the blowing of excessive hot air through the channels to remove the vapor can cause the coating medium to also rise within the channels and thereby change the coating profile.

In one aspect of the present disclosure, the vapor contained within the channels after the coating medium has been applied is drawn out of the channels through the imposition of a vacuum applied at the top end of the substrate alone or in combination with hot air being blown into the bottom end of the substrate. In another aspect, after the coating medium has been applied to one end of the substrate, the substrate can be flipped and excess coating medium can then be blown through the opposite end of the substrate, e.g., using a blast of pressurized air from an air cannon, followed by drying.

A calcination module as generally disclosed herein comprises an apparatus configured and dimensioned to receive a catalytic substrate and can provide operative engagement of a heating apparatus and a blowing device for forcing a gas (e.g. heated air) through the substrate. Forcing hot air through the substrate removes liquid material and the apparatus can further calcine material deposited on the surface of the interior cell walls of the catalytic substrate. As such, embodiments of the calcining apparatus generate hot air or gas and introduce the hot air or gas into a catalytic substrate to evaporate the liquid component of a washcoat comprising a catalytic precursor and/or slurry material and a liquid carrier, and then bringing the impregnated catalytic substrate up to a temperature sufficient to bake the catalytic precursor and/or catalytic slurry onto the cell walls of the catalytic substrate.

Embodiments of the present invention relate to an apparatus that can heat a catalytic substrate in a reduced amount of time sufficient to raise the substrate temperature to a value at which the coating and substrate will dry before the wet coating media may move downward along the walls of the substrate cells under the force of gravity.

The calcination module holds the catalytic substrate within an enclosed chamber, and utilizes a heating fluid to heat the interior of the substrate up to a calcining temperature. In various embodiments, a catalytic substrate is received by a substrate-receiving portion of the calciner, and a short blast of hot gases passed through the substrate cells to raise the temperature of the substrate and calcine any catalytic materials previously deposited on the cell walls. In various embodiments, the catalytic substrate may be de-greened by introducing water vapor into the entry conduit at an intended operating temperature. In one or more embodiments, the catalytic substrate is heated from the inside out by passing hot gas(es) through the cells of the substrate without the hot gas(es) passing around the outside surface of the substrate. In various embodiments, a radial temperature gradient created by heating the catalytic substrate from the outside in apparently contributes to longitudinal and radial stresses which become most evident upon cool down. Thermally induced stress and thermal shock can create cracks and other structural damage to the substrate.
Embodiments of the present invention relate to an apparatus that can supply a heating fluid to a catalytic substrate in a reduced amount of time sufficient to raise at least the internal temperature of the catalytic substrate to a value at which the washcoat will calcine, while reducing or avoiding the amount of thermal shock produced in the substrate.

Certain principles and embodiments of the present invention relate to a system for removing a liquid carrier from a catalytic coating on the inside walls of a monolithic catalytic substrate comprising passing a drying fluid through the cells of the catalytic substrate at a volumetric flow rate of about 200 acfm to about 400 acfm at a temperature in the range of about 100°C to about 115°C (about 212°F to about 239°F) for a time in the range of 5 seconds to about 30 seconds, drying the catalytic substrate at a temperature in the range of about 170°C to about 235°C (about 338°F to about 455°F) for a time in the range of 5 seconds to about 30 seconds, and calcining the catalytic substrate at a temperature in the range of about 350°C to about 425°C (about 662°F to about 797°F) for a time in the range of 5 seconds to about 30 seconds. The drying fluid can be, e.g., air, a combination of air and combustion gases, or a single gas, such as dry nitrogen.

Some principles and embodiments of the present invention relate to a system for affixing a catalytic coating on the inside walls of a monolithic catalytic substrate comprising evaporating the liquid carrier from the catalytic substrate at a temperature in the range of about 100°C to about 115°C (about 212°F to about 239°F) for a time in the range of 5 seconds to about 30 seconds, drying the catalytic substrate at a temperature in the range of about 170°C to about 235°C (about 338°F to about 455°F) for a time in the range of 5 seconds to about 30 seconds, and calcining the catalytic substrate at a temperature in the range of about 350°C to about 425°C (about 662°F to about 797°F) for a time in the range of 5 seconds to about 30 seconds.

In one or more embodiments, the catalytic substrate may have been calcined at a temperature in the range of about 350°C to about 550°C (about 662°F to about 1022°F) for a time in the range of 7 seconds to about 15 seconds, or about 375°C to about 540°C (about 707°F to about 1004°F) for a time in the range of 7 seconds to about 15 seconds. In various embodiments, the calcination temperature is at least 301°C (575°F). In various embodiments, the catalytic substrate temperature increases from room temperature to about 210°C to evaporate the liquid carrier, and from about 301°C to about 540°C to calcine the slurry solids. In one embodiment, on-line calcination with full decomposition of the washcoat can be generally carried out at a temperature of from about 400°C to about 550°C using the systems disclosed herein.

In one or more embodiments, the liquid carrier may have been removed from a catalytic substrate by evaporating the liquid carrier at a temperature in the range of about 105°C to about 110°C (about 212°F to about 230°F) for a time in the range of 15 seconds to about 23 seconds, drying the catalytic substrate at a temperature in the range of about 200°C to about 207°C (about 392°F to about 405°F) for a time in the range of 15 seconds to about 23 seconds, and calcining the catalytic substrate at a temperature in the range of about 395°C to about 405°C (about 743°F to about 761°F) for a time in the range of 7 seconds to about 14 seconds. In various embodiments, the catalytic substrate is dried prior to calcining.

In one or more embodiments, the catalytic substrate may have been calcined at a temperature in the range of about 465°C to about 470°C (about 869°F to about 878°F) for a time in the range of 8 seconds to about 12 seconds. In one or more embodiments, the catalytic substrate may have been calcined at a temperature in the range
of about 535°C to about 540°C (about 995°F to about 1004°F) for a time in the range of 8 seconds to about 12 seconds.

Such a calcination apparatus can includes a central supporting assembly to support the substrate during calcination, which assembly can include a supporting housing with upper and lower sealing gaskets, providing a fluid tight seal around the substrate. The gaskets can be made from any appropriate gasket material which affords a high temperature seal. One useful exemplary gasket is high temperature silicone rubber that can withstand the operating temperatures of the calcination apparatus. The specific components of various embodiments of the calcination apparatus are described in further detail herein below.

Various exemplary embodiments of the invention are described in more detail with reference to the figures. It should be understood that these drawings only illustrate some of the embodiments, and do not represent the full scope of the present invention for which reference should be made to the accompanying claims.

FIG. 1 illustrates an exemplary embodiment of a calcining system 100 in an open position. In one or more embodiments, an inline calciner 100 may comprise a substrate-receiving portion 101 comprising a upper calciner section 110 that is configured and dimensioned to fit over at least a portion of a catalytic substrate 200, and a lower calciner section 120 that is configured and dimensioned to fit over at least a portion of a catalytic substrate 200 to form an enclosed chamber. In various embodiments, the lower calciner section 120 fits over approximately a lower half of the catalytic substrate 200, and the upper calciner section fits over approximately an upper half of the catalytic substrate, when the catalytic substrate 200 is positioned vertically and horizontally so the longitudinal axis of the catalytic substrate is aligned with the longitudinal axis of the upper and lower calciner sections.

In one or more embodiments, the upper calciner section 110 and lower calciner section 120 are coaxial, and may move longitudinally relative to each other. In various embodiments, the longitudinal motion of the upper calciner section 110 may be controlled by a linear actuator (not shown). In various embodiments, the longitudinal motion of the lower calciner section 120 may be controlled by a linear actuator (not shown). In various embodiments, the upper calciner section 110 and/or lower calciner section 120 move linearly between an open position and a closed position.

In one or more embodiments, the catalytic substrate may have a circular cross-section, a rectangular cross-section, or a square cross-section, with a width, diagonal distance, or diameter in the range of about 2 inches to about 14 inches, and a length (height) in the range of about 2 inches to about 12 inches. In various embodiments, the catalytic substrate may have a width, diagonal distance, or diameter in the range of about 3 inches to about 7 inches, and a length (height) in the range of about 4 inches to about 8 inches. In various embodiment, the height and largest perpendicular dimension (width, length, diameter) does not exceed 7 inches. In various embodiments, the hollow interior portions of the upper and lower calciner sections are configured and dimension to match the size and shape of the catalytic substrate intended to be held inside.

In one or more embodiments, the upper calciner section 110 comprises an inlet end and an outlet end, where the outlet end may be connected to and in fluid communication with an upper connecting duct 115, wherein the upper connecting duct may allow axial extension of the upper calciner section 110, while
maintaining a fluid-tight path to the outlet end of the upper calciner section 110. In various embodiments, the inlet end of the upper calciner section 110 may be configured and dimensioned to fit over a catalytic substrate and form a fluid-tight seal when in a closed position. In various embodiments, the upper connecting duct 115 may be a bellows or an arrangement of concentric telescoping sleeves and/or ducts. In various embodiments, the inlet end fits over an intended catalytic substrate.

In one or more embodiments, the lower calciner section 120 comprises an inlet end and an outlet end, where the inlet end may be connected to and in fluid communication with a lower connecting duct 125, wherein the lower connecting duct may allow axial extension of the lower calciner section 120, while maintaining a fluid-tight path to the inlet end of the lower calciner section 120. In various embodiments, the outlet end of the lower calciner section 120 may be configured and dimensioned to fit over a catalytic substrate and form a fluid-tight seal when in a closed position. In various embodiments, the lower connecting duct 125 may be a bellows or an arrangement of concentric telescoping sleeves or ducts. In various embodiments, the outlet end fits over an intended catalytic substrate.

In one or more embodiments, the lower connecting duct 125 may be connected to and in fluid communication with a transfer duct 130 that is connected to and in fluid communication with a source duct 140, and the source duct 140 may be connected to and in fluid communication with a heating fluid source 150, wherein the source duct 140, transfer duct 130, and lower connecting duct 125 comprise a delivery duct that defines a flow path for the heating fluid from the heating fluid source 150 to the lower calciner section 120.

In one or more embodiments, the calciner 100 may further comprise a T-duct 145 inserted between the source duct 140 and the transfer duct 130, such that the straight-through portion of the T-duct 145 is connected to and in fluid communication with the source duct 140 at one end and the transfer duct 130 at the opposite end to facilitate heating fluid flow with minimal pressure loss, and the intersecting branch 147 is connected to and in fluid communication with a by-pass duct 170. In various embodiments, the intersecting branch of the T-duct may be perpendicular or at an angle to the straight-through section of the T-duct to facilitate heating fluid flow to the exhaust.

In one or more embodiments, a calcining control valve 135 may be located in the heating fluid flow path after the T-duct 145 and before the lower connecting duct 125 to control the flow of heating fluid to the lower calciner section 120. In various embodiments a calcining control valve 135 may be inserted between the T-duct 145 and the transfer duct 130 to reduce the amount of dead volume between the T-duct and calcining control valve 135, where the calcining control valve 135 may be closed to block the flow of heating fluid to the lower calciner section 120. In various embodiments, the calcining control valve 135 can rapidly open and close (e.g., in less than 2 seconds, or within 1 second, or in less than 1 second) to control heating fluid flow to the lower calciner section 120 and substrate 200.

In one or more embodiments, a by-pass control valve 175 may be located in the heating fluid flow path after the intersecting branch 147 of the T-duct 145 to control the flow of heating fluid to an exhaust. In various embodiments a by-pass control valve 175 may be inserted between the intersecting portion of the T-duct 145 and the by-pass duct 170, where the by-pass control valve 175 may be closed to block the flow of
heating fluid to the exhaust, so the heating fluid is directed to the calcining control valve 135 and/or transfer duct 130.

In one or more embodiments, the by-pass control valve 175 and the calcining control valve 135 may be automatic valves that can be triggered electrically or pneumatically. In various embodiments, the by-pass control valve 175 and the calcining control valve 135 may be triggered approximately simultaneously, so the flow path from the heating fluid source 150 to the lower calciner section 120 may be blocked at approximately the same time that the flow path from the heating fluid source 150 to the by-pass duct 170 is opened. This approximately simultaneous opening and closing of the by-pass control valve 175 and the calcining control valve 135 provides fast switching between the delivery of the heating fluid to a substrate in the calciner and the exhaust without having to power-up or power-down the heating fluid source 150 and/or one or more heating fluid pumps 160.

In various embodiments, the by-pass control valve 175 and/or the calcining control valve 135 may be cooled by passing cold air over the bearings.

In one or more embodiments, a heating fluid may be provided by a heating fluid source 150. In various embodiments, the heating fluid source 150 may comprise a combustion chamber 151 in which a fuel is burned in an incoming stream of air to produce a high temperature exhaust gas as the heating fluid. In various embodiments, the fuel may be natural gas introduced into the combustion chamber through a fuel line 157 to a burner 158. In various embodiments, an air inlet 155 may provide flow path for air for the combustion process, where the air inlet 155 may be coaxial with the fuel line 157 and/or burner 158. The air may be provided to the air inlet 155 by a heating fluid pump.

In various embodiments, the heating fluid provided by the heating fluid source 150 may be an exhaust gas having a temperature in the range of about 400°C to about 550°C, in the range of about 450°C to about 550°C, or in the range of about 450°C to about 540°C. In various embodiments, the heating fluid source produces in the range of about 150,000 BTU (158,258,378 joules) to about 200,000 BTU (211,011,171 joules). In one or more embodiments, the heating fluid may be a gas comprising oxygen (%), nitrogen (N₂), and carbon dioxide (CO₂). In various embodiments, the heating fluid may be a gas comprising oxygen (%), nitrogen (N₂), carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxides (NOₓ), and water (H₂O). In particular embodiments, the heating fluid may be air, a combination of air and combustion gases, or a single gas, such as dry nitrogen. Under various operating conditions, NOₓ and/or CO may be delivered to a catalytic substrate as part of the heating fluid, wherein the NOₓ and/or CO may react with the catalytic material(s) deposited on the catalytic substrate to produce an exothermic reaction that further increases the temperature of the substrate.

In one or more embodiments, the incoming air stream may be provided to the heating fluid source 150 by one or more heating fluid pump(s) 160 in fluid communication with the heating fluid source 150 through an air infeed duct 165 and/or air inlet 155. In various embodiments, the heating fluid pump(s) 160 may be a blower or a compressor that can deliver air at a suitable flow rate and at a suitable pressure to the combustion chamber 150. In various embodiments, the blower or compressor produces a volumetric flow rate in the range of about 50 scfm to about 150 scfm, while maintaining a pressure in the range of 5 inWG to...
20 inWG. The heating fluid volumetric flow rate and pressure is sufficient to at least propel the heating fluid through the heating fluid source 150, the ductwork 130,140,145, the valve 135, the substrate receiving portion 101, and a substrate 200 to the exhaust.

In one or more embodiments, a heating fluid pump 160 is connected to and in fluid communication with a heating fluid duct 165, and the heating fluid duct 165 may be connected to and in fluid communication with a heating fluid source 150, wherein the heating fluid duct 165 defines a flow path for the heating fluid from the heating fluid pump 160 to the heating fluid source 150. In various embodiments, the heating fluid is air introduced into a combustion chamber 151, in which the air interacts with the fuel being combusted and additional combustion gases are introduced into the heating fluid.

In one or more embodiments, a heating fluid pump (not shown) is connected to and in fluid communication with an air inlet 155, and the air inlet 155 may be connected to and in fluid communication with a heating fluid source 150, wherein the air inlet 155 defines a flow path for air from the heating fluid pump to the heating fluid source 150.

In various embodiments, the various ducts and components, for example, the heating fluid duct 165, source duct 140, T-duct 145, transfer duct 130, lower connecting duct 125, upper calciner section 110, lower calciner section 120, and upper connecting duct 115 may be made of aluminum, steel, or stainless steel, where the material of construction is sufficient to handle the intended operating temperature of the particular duct or component.

The ducts may be thin-walled channel, tubing, and/or flexible tubing (e.g., bellows type). The ducts may have circular, square, rectangular, or other geometrical shaped cross-sections, but for convenience may be referred to as round or circular ducts herein. While particular duct sections and components may be separately identified and labeled, it should be understood that different sections of duct may be combined or fabricated into single unitary sections or further subdivided into smaller sections that may be commercially available or for ease of assembly, and such changes in construction and assembly are considered to be within the scope of the invention as set forth herein and in the claims. In addition, while particular duct sections and components are illustrated as being straight, curved, or having a relative size as illustrated, such depictions are intended for ease of presentation and discussion, and not intended to limit the principles or scope of the invention, for which reference should be made to the claims.

In various embodiments, the incoming air stream may be provided by two heating fluid pumps 160, where one of the heating fluid pumps 160 is a high capacity pump that provides greater than 50% of the heating fluid flow volume, and the other heating fluid pump is a lower capacity pump that provides less than 50% of the heating fluid flow volume, but provides more accurate flow control. In various embodiments utilizing two fluid pumps, the pumps may produce the same pressure to reduce or avoid back-flow in a lower pressure section of the ducts and/or components. In a non-limiting example, a high capacity heating fluid pump may be a gas process blower, and the lower capacity heating fluid pump 160 may be a Cincinnati Blower equipped with a variable frequency drive.

In various embodiments the heating fluid pump may further comprise a differential pressure controller 162 and pressure transducer(s) 168 to maintain a constant flow rate for a pressure drop of 10
inWG (inches water gauge). The differential pressure controller 162 may adjust the heating fluid pump to propel more or less heating fluid through the heating fluid source depending on measured pressure difference.

In various embodiments, the output of the heating fluid pump(s) can overcome the pressure drops introduced by the components of the inline calciner and propel the heating fluid through the calcining system 100 and the substrate 200. In various embodiments, the output of the heating fluid pump(s) 160 is adjusted by the differential pressure controller 162 in electrical communication with the heating fluid pump(s) 160 and pressure transducer(s) 168. In various embodiments, two pressure transducers 168 are installed in the substrate-receiving portion 101 of the calciner, where one transducer is installed before the catalytic substrate and one transducer is installed after the substrate to measure the pressure drop introduced by the substrate. A first pressure transducer 168 may be inserted into the heating fluid flow at the lower connecting duct 125 or lower calciner section 120 to measure the heating fluid pressure before entering the channels of the catalytic substrate, and a second pressure transducer 168 may be inserted into the heating fluid flow at the upper connecting duct 115 or upper calciner section 110 to measure the heating fluid pressure after exiting the channels of the catalytic substrate 200.

In various embodiments, the one or more heating fluid pumps provide sufficient pressure to overcome the pressure drop introduced by a catalytic substrate held with the substrate-receiving portion 101 of the calciner, and deliver the hot heating fluid at a flow rate sufficient to raise the temperature of the catalytic substrate to the calcining temperature within the 0.5 second to 12 seconds of processing, or 7 seconds to 10 seconds of processing, or 9 seconds to 10 seconds of processing cycle time. In various embodiments, the pressure drop introduced by the catalytic substrate is in the range of about 6 inWC (water column) to about 12 inWC, or about 8 inWC to about 10 inWC, or about 10 inWC.

In various embodiments, the heating fluid source 150 is a hot air combustion system comprising a combustion chamber 151, a fuel line 157, and a burner 158, which may be a gas burner, a fuel oil or diesel fuel burner, or kerosene burner. In various embodiments, the burner may be multi-fuel burner connected to a suitable fuel source. In various embodiments, the heating fluid source 150 comprises a combustion chamber 151 and a gas burner.

In various embodiments, the monolithic catalytic substrate may be in the calciner for a period of time in the range of about 0.5 seconds to about 4 seconds, or alternatively between about 1 second and about 2 seconds, or alternatively between about 2 seconds and about 3 seconds, or for about 1.5 seconds. In one or more embodiments, the calcining system 100 may comprise a water reservoir 190 for storing and providing water to the heating fluid. In various embodiments, the water may be pumped by a water pump 180 from the reservoir 190 to a water injection nozzle 185 inserted into a section of the source duct 140 to deliver a water spray or mist into the hot heating fluid flow. The water injection nozzle 185 is connected to and in fluid communication with a water pump 180 and the water reservoir 190. The injected water may be volatilized and conveyed with the hot heating fluid to de-green a catalytic substrate while it is being calcined. In various embodiments, the water reservoir 190 may have sufficient capacity to store and provide 40 lbs./hour of water for at least 1 hour, at least 2 hours, at least 4 hours, or at least 8 hours to the to the
water injection nozzle 185 without being refilled. In various embodiments, the water may be deionized water. In various embodiments, the heating fluid from the heating fluid source and the vaporized water is conveyed to the inlet end of the lower calciner section through a delivery duct comprising a source duct 140, a transfer duct 130, and a lower connecting duct 125. In various embodiments, the delivery duct may further comprise a T-duct 145 and/or a calcining control valve 135.

In one or more embodiments, a catalytic substrate may be de-greened by passing a heating fluid comprising combustion gases at a temperature in the range of about 450°C to about 550°C having a humidity in the range of 4% to about 15%, or in the range of about 5% to about 15%, or about 10% to about 15% through the plurality of longitudinal cells of the catalytic substrate, so the combustion gases react with the catalytic material and carrier liquid to produce a chemical reaction that de-greens the catalytic substrate. In various embodiments, a catalytic substrate may be processed for about 8 seconds to about 10 seconds to de-green the catalytic substrate.

In one or more embodiments, the water pump may feed 0.05 to 0.2 gallons per minute (GPM), or about 0.1 GPM, of water to the source duct 140, where the water is injected as a spray or mist into the hot heating fluid. In various embodiments, the water injection increases the humidity of the heating fluid from about 4-5% to about 10-15%.

In one or more embodiments, a safety interlock comprising a water pump controller 187 in electrical communication with the water pump 180 and at least one temperature sensor 188 to detect the temperature of the heating fluid in the source duct 140, wherein the interlock prevents the water pump from operating and shuts the water pump 180 off if the temperature of the heating fluid and/or source duct 140 detected by the temperature sensor 188 is below the intended operating temperature.

In various embodiments, the intended operating temperature of the heating fluid for water injection is in the range of about 450°C to about 550°C, and the heating fluid source may be at least 165,000 BTU, or at least 200,000 BTU or at least about 225,000 BTU.

In one or more embodiments, one or more electrical heaters may be affixed to the exterior of the duct(s) 140, 145, 130 at and/or downstream from the point the water is injected into the heating fluid flow to raise the temperature of the duct(s) to reduce or avoid cooling of the duct after the point of water injection and condensation of the water on the interior duct surfaces. One or more electrical heaters may be affixed to the exterior of the source duct 140 at and/or downstream from the point the water is injected. One or more electrical heaters may also be affixed to the exterior of the T-duct 145 at and/or downstream from the point the water is injected into the heating fluid flow to raise the temperature of the T-duct. In various embodiments, a drain valve may be installed in the source duct 140 to allow drainage of condensed water. In various embodiments, internal fins and/or pins may be provided within the source duct 140, and in thermal contact with the interior surface of the source duct 140 and/or electrical heaters, to provide increase surface area for thermal transfer to the injected water. In one or more embodiments, the electrical heater(s) may provide 15 kW to 20 kW, or about 18 kW to the duct.

In one or more embodiments, a steam jacket connected to and in fluid communication with a steam source (e.g., boiler) may be affixed to the exterior of the duct(s) 140, 145, 130 at and/or downstream from the
point the water is injected into the heating fluid flow to raise the temperature of the duct to reduce or avoid cooling of the duct after the point of water injection and condensation of the water on the interior duct surfaces.

In various embodiments, the coating solution may comprise a soluble catalytic precursor and/or catalytic slurry material. In various embodiments, the coating solution may comprise platinum group metals and/or base metals, one or more ceramic support material(s) and/or zeolites, and a carrier fluid, where the carrier fluid may comprise acetic acid.

In one or more embodiments, a scale may be operatively associated with the calcining apparatus to determine the wet weight of a catalytic substrate after the application of the coating liquid to the catalytic substrate. A measure of the additional weight of the catalytic substrate after application of the washcoat may be calculated by the difference between the initial dry weight of the substrate and the wet weight measured by respective scales, to determine whether a correct amount of coating liquid was applied. In one or more embodiments, a scale may be operatively associated with the calcining apparatus to determine the weight of a catalytic substrate prior to the calcining of the washcoat to the face of the substrate cell walls. In various embodiments, a scale may be operatively associated with the calciner to determine if the post-calcining weight falls within intended limits. If it is determined that a catalytic substrate has a weight after calcining that is outside intended limits, the catalytic substrate processing may be interrupted to allow adjustments, calibrations, and/or maintenance before additional substrates that may be out of specification are produced.

In various embodiments, the catalytic substrate may be weighed on a first scale to obtain an intermediate or wet weight prior to calcining, wherein the scale may comprise a computer and/or a memory configured to receive and store weight values obtained for a catalytic substrate, or the scale may be in electronic communication with a computer and/or a memory configured to receive and store weight values obtained for a catalytic substrate. The catalytic substrate may be removed from the calcining apparatus and placed on a second scale by a robot. In various embodiments, the transfers between one or more of the processing stations (e.g., staging area(s), weigh station(s), statistical processing control station(s), cooling stations, etc.) may be done by a person instead of a robot.

In various embodiments, the concentration of the coating solution may be between about 0.5% and about 5% by weight of platinum group metal, or alternatively, the coating solution may have a concentration of between about 1% and about 2% by weight of platinum group metal, or about 1.5% by weight of platinum group metal. In various embodiments, the coating solution comprises platinum, which may be a soluble compound dissolved in a liquid carrier. The soluble platinum compound may be for example, chloroplatinic acid, platinum (IV) chloride, K₂PtCl₄, and platinic sulfates.

FIG. 2 illustrates an exemplary embodiment of the calciner 100 in which an upper calciner section 110 and lower calciner section 120 of the substrate-receiving portion 101 are in a closed position encasing the catalytic substrate 200, so that hot heating fluid conveyed from the heating fluid source 150 through the lower connecting duct 125 enters the interior volume of a transitional section 123, and passes through the plurality of longitudinal cells of the catalytic substrate to the upper calciner section 110.
In an embodiment, the upper connecting duct 115 and the lower connecting duct 125 may comprise two or more concentric sleeves arranged in a telescoping manner to provide for linear movement of the upper calciner section 110 and lower calciner section 120, wherein the upper calciner section and/or lower calciner section may be moved linearly to encase the catalytic substrate.

In one or more embodiments, the upper connecting duct 115 may comprise at least an outer sleeve 117 and an inner sleeve 118, wherein the inner sleeve 118 and outer sleeve 117 are configured an dimension to allow the inner sleeve to fit within and slidably engage the outer sleeve when the upper calciner section 110 and lower calciner section 120 are in an open position for receiving a catalytic substrate.

In one or more embodiments, the upper connecting duct 115 may comprise an outer sleeve 117, an inner sleeve 118, and one or more intermediate sleeves configured and dimensioned to fit concentrically between and be slidably engaged with the outer sleeve 117 and inner sleeve 118, so as to provide axial telescoping movement of the sleeves.

In one or more embodiments, the lower connecting duct 125 may comprise at least an outer sleeve 127 and an inner sleeve 128, wherein the inner sleeve 128 and outer sleeve 127 are configured an dimension to allow the inner sleeve to fit within and slidably engage the outer sleeve when the upper calciner section 110 and lower calciner section 120 are in an open position for receiving a catalytic substrate.

In one or more embodiments, the lower connecting duct 125 may comprise an outer sleeve 127, an inner sleeve 128, and one or more intermediate sleeves configured and dimensioned to fit concentrically between the outer sleeve 127 and inner sleeve 128, so as to provide axial telescoping movement of the sleeves. In one or more embodiments, the upper connecting duct 115 and/or the lower connecting duct 125 may be bellows that provide a fluid-tight flow path.

In operation, a catalytic substrate may be placed between the upper calciner section 110 and lower calciner section 120, when the two sections are in an open position, as shown in FIG. 1, where the catalytic substrate is axially aligned with and vertically positioned between the upper and lower calciner sections.

The upper calciner section 110 and lower calciner section 120 may be coaxial, so longitudinal movement of the upper and lower calciner sections will close around the substrate without experiencing interference with the outer edges and surfaces of the catalytic substrate.

In various embodiments, the substrate-receiving portion 101 is configured and dimensioned to have sufficient axial movement to provide clearance between a lower edge of an upper calciner housing 111 and an upper edge of a lower calciner housing 121 for a catalytic substrate having an particular height to be moved horizontally into position by a robot, and aligned with the axis of the upper calciner section 110 and lower calciner section 120. The clearance between a lower edge of an upper calciner housing 111 and an upper edge of a lower calciner housing 121 is sufficient to avoid collision between the catalytic substrate and the sides and/or edges of the upper calciner housing 111 and lower calciner housing 121, when the catalytic substrate is being moved into or out of position.

In one or more embodiments, the pressure transducer(s) 168 may be operatively associated with the lower calciner section 120 to measure the heating fluid pressure before entering the channels of the catalytic substrate and the upper calciner section 110 to measure the heating fluid pressure after exiting the channels.
of the catalytic substrate 200. The two pressure measurements from the pressure transducers 168 may be used to calculate a differential pressure across the substrate being calcined by the differential pressure controller 162, which may adjust the flow and/or pressure of the heating fluid being provided by the heating fluid pump(s) 160 to maintain the intended heating fluid flow through the substrate 200. In various embodiments, the heat produced by the heating fluid source 150 may be adjusted to compensate for changes in the heating fluid flow to maintain the intended calcining temperature.

FIG. 3 illustrates an exemplary embodiment of an inline calcining system 100 depicting a substrate-receiving portion 101 in a closed position against a substrate gripper assembly 300. In one or more embodiments, the upper calciner section 110 closes against a top face and lower calciner section 120 closes against a bottom face of the gripper assembly 300 to inhibit flow of heating fluid around the outside of the catalytic substrate 200. In various embodiments, the clearance between the inside surface of the upper calciner section 110 and the outer surface of the catalytic substrate 200 is .125 inches or less. In various embodiments, the clearance between the inside surface of the lower calciner section 120 and the outer surface of the catalytic substrate 200 is 0.125 inches or less.

In one or more embodiments, the upper connecting duct 115 and/or the lower connecting duct 125 comprise thin-walled bellows that provide a fluid-tight seal between the interior volume and ambient atmosphere during longitudinal movement of the upper calciner section 110 and/or lower calciner section 120. The bellows forming the upper connecting duct 115 provides a fluid-tight flow path between the upper calciner section 110 and the exhaust duct 119. The bellows forming the lower connecting duct 125 provides a fluid-tight flow path between the lower calciner section 120 and the transfer duct 130.

In one or more embodiments, the heating fluid may flow through an exhaust duct to be evacuated to the atmosphere. In various embodiments, the heating fluid may flow through a catalytic substrate to the upper calciner section 110, to the upper connecting duct 115, to the exhaust duct 119, and to a scrubber and/or catalytic converter to remove combustion products (NOx, CO, hydrocarbons, etc.) from the heating fluid before venting to the atmosphere.

In various embodiments, the heating fluid source 150 may comprise a heat exchanger 156 operatively associated and in fluid communication with a combustion chamber 151 having a fuel line 157 and burner 158, where the combustion gas from the combustion chamber heats an internal portion of the heat exchanger, and the heating fluid provided by heating fluid pump 160 passes across the heat exchanger internals to become heated to the intended operating condition. The use of a heat exchanger separates the combustion gases from the heating fluid, which may be air or a mixture of air and other gases.

FIG. 4 illustrates an exemplary embodiment of an inline calcining system 100 depicting a substrate-receiving portion 101 in a closed position. In one or more embodiments, the upper calciner section 110 and/or lower calciner section 120 may comprise a bellows that allows the portion of the upper calciner section 110 and/or lower calciner section 120 to move longitudinally, while the upper connecting duct 115 and/or the lower connecting duct 125 remain stationary. In various embodiments, a lower edge of the bellows forming the upper calciner section 110 closes against a top face of the gripper assembly 300, and an upper edge of the bellows forming the lower calciner section 120 closes against a bottom face of the gripper.
assembly 300. In various embodiments, the bellows portion of the upper calciner section 110 and/or lower calciner section 120 may be moved longitudinally by a linear actuator.

FIG. 5 illustrates an exemplary embodiment of an upper calciner section 110 and a lower calciner section 120. In one or more embodiments, an upper calciner section may comprise a housing 111 having an outer wall 112 and an interior area 116 comprising an open volume, wherein the interior area 116 may be configured and dimensioned to fit over at least a portion of a catalytic substrate 200. In various embodiments, the clearance between the inside surface of the lower calciner section 120 and the outer surface of the catalytic substrate 200 is 0.0625 inches or less, and the clearance between the inside surface of the upper calciner section 110 and the outer surface of the catalytic substrate 200 is 0.0625 inches or less.

In various embodiments, the interior area 116 may have a cylindrical shape, a rectangular shape, a shape, a hexagonal shape, a triangular shape, or other geometric shapes, which may conform to a catalytic substrate having a particular shape. In various embodiments, the outer wall 112 of the upper calciner housing 111 may have a cylindrical shape, a rectangular shape, a square shape, a hexagonal shape, a triangular shape, or other geometric shapes, wherein the outer wall 112 of the upper calciner section housing 111 may have a shape, which may conform to the particular shape of the interior area 116.

In one or more embodiments the upper calciner section housing 111 may further comprise a transitional section 113 having an outer wall 114, wherein the outer wall 114 of the transitional section 113 may be connected to the outer wall 112 of the upper calciner housing 111. In various embodiments the outer wall 114 of the transitional section 113 may be joined to the outer wall 112 of the upper calciner section housing 111 for example by welding, or by mechanical fastening, or the outer wall 114 of the transitional section 113 and the outer wall 112 of the upper calciner housing 111 may be formed from the same piece of material to have a unitary construction.

In one or more embodiments, the transitional section 113 may have an inside diameter at a first end and an inside diameter at a second end opposite the first end, wherein the inside diameter at the second end is smaller than the inside diameter of the first end. In various embodiments, the outer wall 114 of the transitional section 113 tapers from the first end to the second end. In various embodiments, transitional section 113 may comprise a series of step-wise reductions in the inside diameter between the first end and the second end. In various embodiments, the first end of the transitional section 113 is the end connected to the upper calciner housing 111. In various embodiments, a pressure transducer 168 may be operatively associated with transitional section 113.

In one or more embodiments the lower calciner section housing 121 may further comprise a transitional section 123 having an outer wall 124, wherein the outer wall 124 of the transitional section 123 may be connected to the outer wall 122 of the lower calciner housing 121. In various embodiments the outer wall 124 of the transitional section 123 may be joined to the outer wall 122 of the upper calciner section housing 121 for example by welding, or by mechanical fastening, or the outer wall 124 of the transitional section 123 and the outer wall 122 of the upper calciner housing 121 may be formed from the same piece of material to have a unitary construction.
In one or more embodiments, the transitional section 123 may have an inside diameter at a first end and an inside diameter at a second end opposite the first end, wherein the inside diameter at the first end is smaller than the inside diameter of the second end. In various embodiments, the outer wall 124 of the transitional section 123 tapers from the first end to the second end. In various embodiments, transitional section 123 may comprise a series of step-wise reductions in the inside diameter between the first end and the seconds end. In various embodiments, the second end of the transitional section 123 is the end connected to the lower calciner housing 121. In various embodiments, a pressure transducer 168 may be operatively associated with transitional section 123.

In one or more embodiments, an upper calciner section housing 111 and a lower calciner section housing 121 may comprise a tubular wall with a circular cross-section, as shown in FIG. 5A, having a height, wherein the height is sufficient to cover approximately half of the length of a catalytic substrate, and a cylindrical interior area forming an open interior volume sized to receive at least a portion of a catalytic substrate.

In one or more embodiments, an upper calciner section housing 111 and a lower calciner section housing 121 may comprise a tubular wall with a rectangular cross-section, as shown in FIG. 5B, having a height, wherein the height is sufficient to cover approximately half of the length of a catalytic substrate, and a cylindrical interior area forming an open interior volume sized to receive at least a portion of a catalytic substrate.

In various embodiments, the catalytic substrate 200 may be loaded into the system robotically or by hand. In one or more embodiments, the robotic transfer element may comprise a catalytic substrate gripper assembly 300, to grip and transport each substrate.

FIG. 6A illustrates a top view of an exemplary embodiment of a gripper assembly 300 for holding a catalytic substrate. In various embodiments, the catalytic substrate gripper comprises two C-shaped rings 310 having an inside diameter sized to fit an intended catalytic substrate. In various embodiments, the insert 320 in each of the two C-shaped rings 310 is compressible and forms a fluid-tight seal around the outer shell of a catalytic substrate, when the substrate is being gripped. The gripper assembly may further comprise an arm 330 operatively associated with each of the C-shaped rings 310 to manipulate the rings and move a held substrate.

FIG. 6B illustrates a front cut-away view of an exemplary embodiment of a gripper assembly 300 for holding a catalytic substrate. In one or more embodiments, the catalytic substrate gripper assembly comprises a silicone rubber insert 320 that can operate continuously at a temperature of at least 600°F. In various embodiments, the insert and clamp assembly act as an insulator and heat sink for a short exposure time of <16 seconds.

In one or more embodiments, the catalytic substrate may be held in horizontal and vertical position by a catalytic substrate gripper assembly 300, while upper calciner section 110 and lower calciner section 120 move longitudinally to envelope the catalytic substrate 200, where the lower edge of the outer wall 112 of the upper calciner section housing 111 contacts a top face of the catalytic substrate gripper assembly, and
the upper edge of the outer wall 122 of the lower calciner section housing 121 contacts a bottom face of the catalytic substrate gripper assembly 300.

In various embodiments, the lower edge of the outer wall 112 forms a fluid-tight seal with the top face of the two C-shaped rings 310 of the catalytic substrate gripper assembly 300, and the upper edge of the outer wall 122 forms a fluid-tight seal with the bottom face of the two C-shaped rings 310 of the bottom face of the catalytic substrate gripper assembly 300.

In one or more embodiments, the heating fluid flows through the lower calciner section 120 into the channels of the catalytic substrate, and through the catalytic substrate to the upper calciner section 110. In various embodiments, the fluid-tight seals between the gripper rings 310 and the outer surface of the substrate 200, and the fluid-tight seals formed between the outer walls of the calciner housings and the top and bottom surfaces of the gripper rings 310, prevents the heating fluid from flowing around the catalytic substrate. The insert may be exposed to the hot heating fluid during a processing cycle, and the temperature of the catalytic substrate, so is adapted to withstand the temperature to which it is exposed.

In various embodiments, the clearance between the inside surface of the upper calciner housing and the outer surface of the catalytic substrate calciner is minimized to reduce the amount of dead volume and heating fluid flowing along the outside of the catalytic substrate.

In one or more embodiments, the lower calciner section 120 may be connected to and in fluid communication with a lower connecting duct 125, wherein the lower connecting duct may allow axial extension of the lower calciner section 120, while maintaining a fluid-tight path to the lower calciner section 120. In various embodiments, the lower connecting duct 125 may be a bellows or an arrangement of concentric telescoping sleeves and/or ducts.

FIG. 7 illustrates an exemplary embodiment of a method of calcining a catalytic substrate. Principles and embodiments of the present invention relate to a method of affixing and calcining a catalytic coating to one or more faces of the cells of a catalytic substrate, wherein at least one catalytic coating may have been previously dried onto the interior of the catalytic substrate cells.

At 710 a flow of heating fluid is provided by a heating fluid pump to a combustion chamber. In one or more embodiments, a heating fluid pump may be brought from an off state to an operating output of about 10% to about 20% of the pump's total output to deliver a flow of air/heating fluid to the combustion chamber. The air flow should be sufficient to allow combustion in the combustion chamber.

At 720 a fuel is provided to the combustion chamber and allowed to mix with the air/heating fluid in a ratio sufficient to ignite and burn the fuel. The flow of fuel to the burner may be increased to generate an intended amount of heat (BTUs). The fuel-heating fluid mixture is ignited to produce a heating fluid at a higher temperature intended for calcining one or more catalytic substrates. The temperature of the heating fluid is increased to an intended temperature by the heating fluid source.

At 730 the bypass valve is opened to allow heating fluid that is not yet at the intended calcining temperature and/or of an insufficient flow rate to escape through the by-pass duct to an exhaust. In various embodiments, the by-pass duct may be in fluid communication with a scrubber and/or catalytic converter to
remove combustion products (NO\textsubscript{x}, CO, hydrocarbons, etc.) from the heating fluid before venting to the atmosphere.

At 740, the heating fluid pump(s) is increased to 100% of total output. The burner output may also be increased to maintain sufficient combustion and heating fluid temperature.

At 750, a catalytic substrate is positioned within the substrate-receiving portion 101, and axially aligned with the upper calciner section 110 and lower calciner section 120. The catalytic substrate may be held by a gripper assembly and moved into proper position by a robot.

At 760, the upper calciner section may be lowered over the positioned catalytic substrate, and/or the lower calciner section may be raised over the catalytic substrate. In various embodiments, the upper calciner section or lower calciner section may remain in a fixed position and the opposite section raised or lowered completely over the catalytic substrate, where at least one calciner section 110,120 has sufficient height and travel to cover the entire catalytic substrate. The upper calciner section and/or lower calciner section are moved linearly to encase the catalytic substrate within the upper calciner section and lower calciner section.

At 770, the calcining control valve is opened and the bypass control valve is closed to allow heating fluid at an intended temperature, pressure, and flow rate to pass through the ducts to the lower calciner section 120, and into the cells of the positioned catalytic substrate. The calcining control valve and the bypass control valve may be adapted to function in tandem to redirect the heating fluid from the lower calciner section to the by-pass duct.

At 780, the hot heating fluid passes through the cells of the catalytic substrate and heats the substrate more uniformly from the inside out, as compared to an oven that may typically heat from the outside in. The temperature and flow rate of heating fluid may be sufficient to raise the substrate temperature to the intended calcining temperature in less than 7 seconds, and process the substrate at the calcining temperature for 1 to 2 seconds.

At 785, the pressures measured by the pressure transducers are used to adjust the output of the heating fluid pump to maintain a constant temperature and flow rate taking into account the pressure drop across the catalytic substrate.

At 790, the water pump is activated to propel the water from a reservoir to a water injection nozzle, where the water is injected into the heating fluid while the catalytic substrate is being processed to de-green the catalytic substrate. The injected water may be vaporized and carried with the heating fluid to the catalytic substrate.

At 795, the calcining control valve is closed and the bypass control valve is opened to allow heating fluid to escape through the by-pass duct to the exhaust. In various embodiments, the temperature, pressure, and flow rate of the heating fluid remain constant when the catalytic substrate is being loaded and unloaded from the substrate-receiving portion to provide faster cycle times than would be achievable by adjusting the heating fluid pump output and/or combustion chamber heat/output. The heating fluid flow is redirected from the lower calciner section to the exhaust.

At 799, the upper calciner section may be raised, and/or the lower calciner section may be lowered a sufficient distance to allow removal of the catalytic substrate. In various embodiments, the upper calciner
section or lower calciner section may remain in a fixed position and the opposite section raised or lowered completely from the catalytic substrate, where at least one calciner section 110,120 has sufficient travel to uncover the entire catalytic substrate.

FIG. 8 illustrates an exemplary embodiment of a method of calcining a catalytic substrate.

At 810, the catalytic substrate is positioned and aligned between upper calciner section and lower calciner section.

At 820, the upper calciner section and/or lower calciner section are moved vertically relative to the stationary catalytic substrate to envelope the substrate and provide a flow path for the heating fluid only through the cells of the catalytic substrate.

At 830 the heating fluid is passed through the cells of the catalytic substrate for a duration and at a temperature sufficient to initiate an exothermic reaction between the gases comprising the heating fluid and the catalytic coating on the walls of the substrate. In various embodiments, the heating fluid temperature may be in the range of 400°C to about 550°C to initiate the exothermic reaction. In various embodiments, the catalytic coating and/or slurry material may comprise a platinum group metal including, platinum, palladium, rhodium, ruthenium, osmium, and iridium, or combinations thereof.

At 840, the upper calciner section and/or lower calciner section are moved vertically relative to the stationary catalytic substrate to expose the substrate after the processing cycle.

At 850, the catalytic substrate is removed from the inline calciner.

At 860, the calcined catalytic substrate may be weighed to determine the final weight of the substrate and catalytic coating.

The operation of the apparatus and methods of using it are understood in conjunction with the drawings and the foregoing description of such drawings. Generally, the upper and lower housings are secured about the substrate so that the respective hoods are sealed to the housing through the respective gaskets. The blower (not shown) can be activated while a hot gas (e.g., hot air) is forced into the conduit. Residual vapors are drawn from the substrate through the upper hood and out the conduit, while hot air can be forced upwardly through the conduit into the lower hood and up into the bottom end of the substrate. As a consequence, the hot air within the channels of the substrate can be pushed through the channels through the upper housing as calcination is carried out. An exemplary heating apparatus is a hot air burner system available from Hauck Manufacturing Co., Lebanon, Pennsylvania, and an exemplary process blower unit is available from Airpro, Rhinelander, Wisconsin.

The operation of the apparatus and methods can be further understood based on the following non-limiting example. In this non-limiting example, a catalytic substrate comprising a dry washcoat layer deposited on a plurality of cell walls is received by an inline calciner, the upper calciner section and lower calciner section move axially to encase the catalytic substrate, a heating fluid having a temperature in the range of about 465°C and about 550°C is passed through the cells of the catalytic substrate at a flow rate in the range of about 200 acfm and about 400 acfm for a time period in the range of about 8 seconds to about 12 seconds to calcine the deposited washcoat on the catalytic substrate.
The calcining station may comprise a substrate-receiving portion comprising an upper calciner section and a lower calciner section, wherein the upper calciner section and the lower calciner section are configured and dimensioned to fit over the catalytic substrate and form a fluid-tight seal against each other or against a gripper assembly, and a heating fluid source that supplies a volume of heating fluid at an intended temperature operatively associated with the lower calciner section, wherein the heating fluid is delivered to an inlet end of the lower calciner section to calcine the catalytic slurry of the washcoat to the cell walls of the catalytic substrate, and a substrate gripper that holds the catalytic substrate and transfers the catalytic substrate between the catalytic substrate coating station, the at least one drying station, and the one or more calcining stations, wherein one calcining station of the one or more calcining stations is adjacent to one of the at least one drying stations.

In various embodiments, the coating system may further comprise a second catalytic substrate coating station that applies at least one additional washcoat comprising a catalytic slurry and a liquid carrier to at least a portion of the catalytic substrate after the catalytic substrate has been calcine at least once at the one or more calcining stations.

In various embodiments, the coating system may further comprise at least one weighing station comprising a scale that measures the weight of the catalytic substrate, wherein the substrate gripper transfers the catalytic substrate from the catalytic substrate coating station, the drying station, or the calcining station to the at least one weighing station to determine a wet, intermediate, and/or a dry weight of the catalytic substrate, where a wet weight is a weight of a substrate coated with a washcoat before any removal of the carrier, an intermediate weight is after at least a portion of the liquid carrier has been removed by drying the substrate and washcoat, and a dry weight may be after essentially all the liquid carrier has been removed by drying or after calcining a coated substrate. The specific substrate employed (i.e., onto which a coating medium is applied and calcined based on the methods, modules, and systems described herein) can vary. In various embodiments, the catalytic substrate comprises a monolithic ceramic or metal honeycomb structure, where the monolithic substrate can have fine, parallel gas flow passages extending longitudinally such that the passages are open to fluid flow there through. The passages, which are essentially straight paths from their fluid inlet to their fluid outlet, are defined by walls on which the catalytic material is coated as a washcoat so that the gases flowing through the passages contact the catalytic material. The flow passages of the monolithic substrate can be 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 900 or more gas inlet openings (i.e. cells) per square inch of cross section.

In one or more embodiments, catalytic substrates include thin porous walled honeycombs monoliths through which the fluid stream passes without causing too great an increase in back pressure or pressure across the article. For example, in some embodiments, the substrate is ceramic. Ceramic substrates may be made of any suitable refractory material, e.g. cordierite, cordierite-a-alumina, silicon nitride, silicon carbide, zircon mullite, spodumene, alumina-silica-magnesia, zircon silicate, sillimanite, a magnesium silicate, zircon, petalite, a-alumina, an aluminosilicate and the like, where such materials are able to withstand the environment, particularly high temperatures, encountered in treating the exhaust streams.
A washcoat, or "coating medium" may be formed by preparing a slurry containing a specified solids content (e.g., 30-90% by weight) of catalyst in a liquid vehicle, which is then coated onto a substrate and dried to provide a washcoat layer. As used herein, the term "washcoat" has its usual meaning in the art of a thin, adherent coating of a catalytic or other material applied to a substrate material, such as a honeycomb-type carrier member, which is sufficiently porous to permit the passage of a gas stream being treated.

The coating medium which can be employed to coat the substrate in accordance with the apparatus and methods described herein vary widely. Catalytic compositions containing precious metals or base metals can be used as well as adsorbent compositions containing pollutant-absorbing materials such as zeolites and the like.

Catalysts which may be included in the composition can vary widely but generally include platinum group metals (PGMs), base metals, alkaline earth metals, rare earth metals, and early transition metals. Some metal catalysts can be soluble compounds dissolved in a liquid carrier (e.g., H₂O). PGMs include platinum, palladium, rhodium, ruthenium, osmium, and iridium, and combinations thereof. Base metals include manganese, vanadium, copper, nickel, cobalt, chromium, tin, iron, silver, gold, and cesium. Alkaline earth metals include beryllium, magnesium, calcium, strontium, barium, and radium. Rare earth metals include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Early transition metals include scandium, yttrium, titanium, zirconium and hafnium.

In various embodiments, the slurry may comprise alumina, silica-alumina, zeolites, zirconia, titania, lanthana, and combinations thereof. In various embodiments, the slurry may comprise oxides of calcium, barium, strontium, cerium, cesium, copper, iron, nickel, cobalt, manganese, chromium, vanadium, and combinations thereof.

EXAMPLES

Example 1 - Thermal Shock to Failure Testing.

Substrate contour (round vs. oval), length (short vs. long), washcoat formulation (low and high % decomposition) and PGM loading (low and high) were explored - see TABLE 1 for On-Line Calcination Data. For a given PGM load, technology and substrate combination, multiple units were coated and dried. Each resulting group was then split into two sets, one calcined on-line and the other calcined through a standard conveyor belt calciner. Three parts from each set were then tested to failure. Upon completion, data from each experimental set was normalized by dividing through by the lowest observed failure temperature. This was carried out for 10 different PGM load, technology, and substrate combinations for a total of 66 data points (33 on-line and 33 off-line through D6, an off-line endpoint). Figures 10A and 10B show the resulting density and failure frequency plots indicating that calcination on-line improved thermal shock parameter. Both graphs show that calcination off-line (D6) produced more low temperature failures compared to those calcined on-line. Thus on-line calcination exhibits thermal shock failures at higher temperatures which is the desired result. This result was unexpected based on the state of the art. After conducting these experiments the reason became clear as temperature control and air flow uniformity were improved via calcination on-line (excellent heat transfer via convection vs. poor heat transfer via conduction.
using current production calciners) - see Figure 11. Calcination on-line has 100% of the heated airflow being directed through the coated unit with a flow rate ca. 290 ACFM (Actual Cubic Feet per Minute).

TABLE 1

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<th>Technology</th>
<th>Type</th>
<th>Part Dimensions (in.)</th>
<th>Cell Density (gpm/\footnote{mil wall thickness})</th>
<th>Unit Vol. (in.³)</th>
<th>PGM Loading (g)</th>
<th>% Wt. Loss (Process to Drying to O/LC)</th>
<th>% Wt. Loss (O/LC to D6) *</th>
<th>Calciner Temp. (°C)</th>
<th>Calciner Dwell (sec)</th>
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Table 1 represents a compilation of technology, substrate dimensions, PGM loading and substrate unit volumes processed under the same drying and calcination conditions. Conditions utilized were:

225/400/400/875°F with a 10.1 second dwell time which equates to an 11 second cycle time on a production coater. Coating weight loss measured between drying and calcination on-line was measured and was observed to be substantial. On-line calcined units were processed again through a standard mass production calciner. In all cases, the additional coating weight change recorded in the % Wt. Loss (OLC to D6) column was negligible and could be attributed to either absorbed water, NO_x or CO_y with NO_x and CO_y associated with designs containing high amounts of Barium. However, in the case of "Technology B" samples, a trend exists which suggests use of thermally fixed Pd can be advantageous. When PGM post addition increased the overall % decomposition also increased. In the case of 50% Pd post addition, it is apparent that slightly less washcoat decomposition took place initially on-line contributing to the highest post treatment loss. This also suggests that thermally fixed Pd is more catalytic towards assisting decomposition of base metal salts in the washcoat compared to soluble PGM salts which must decompose to become catalytically active.
Example 2 - Electron Probe Micro Analysis (EPMA).

Elemental mapping was utilized to determine success in preventing migration of base metals and to determine the minimum calcination temperature requirement. Namely, this test was performed to ensure that migration of elements such as La, Ba, and Sr from bottom coat to top coat layer can be suppressed via calcination on-line. Calcination limits defined for this statistical design of experiments (DoE) (400 - 750°F) were established based trials using LEX-120 tri-metallic catalyst. During this period it was determined that 300°C (ca. 575°F), the center-point of this DoE was required to prevent La migration from bottom to top coat layer.

As part of this current DoE a baseline case was generated using control catalyst samples manufactured by BASF Corp. (Huntsville, Alabama). Control samples were prepared by the traditional process by which Pd and Rh are impregnated separately on an alumina support and then utilized to produce catalytic washcoat slurries. In both cases, impregnated support materials were utilized without any intermediate drying or calcination steps. Via this method, it is known that as much as 80% of the impregnated PGM leaches off the support material to become soluble in the slurry liquid phase. The palladium slurry, which contains base metal salts of La, Ba, Sr, and Zr along with alumina support and bulk Ce/Zr powder, can be then coated, dried and calcined off-line at 550°C to generate a Pd/base metal oxide layer designated as bottom coat. The Rh slurry, which contains salts of Zr, alumina support and bulk Ce/Zr can be then applied over the Pd bottom coat dried and then calcined off-line at 550°C. EPMA of the resulting double coat catalyst is shown in Figures 12A and 12B.

In Figure 12A, the Pd bottom coat and Rh top coat layers are visible. Due to solubility of Rh in the liquid phase, some Rh migrates down into the Pd bottom coat layer. In Figure 12B, which includes Pd, Sr, Ba, and La, it is also apparent that some Sr, Ba, and La leach into the top coat slurry when applied over a calcined bottom coat. Although this is the case, the majority of these base metals do remain in the bottom layer per design.

The next step was to begin evaluating DoE experiments to determine if the same fingerprint could be accomplished using calcination on-line and if so, the minimum temperature requirement to accomplish said goal. Experiment numbers 11 (400°F/200°C), 4 (575°F/300°C), and 8 (750°F/400°C) and were performed to evaluate the center and design end points.

Example 3 - Experiment No. 11 - Low Temperature On-Line Calcination

Starting with experiment 11, it was clear that 400°F/200°C is not high enough to decompose base metal salts of Ba, Sr and La as all have visibly migrated from the bottom to top coat layer. Top coat application has actually solubilized these species to the point of creating a high concentration of each element towards the surface of the top coat - see Figures 13A and 13B.

Example 4 - Experiment No. 4 - Intermediate Temperature On-Line Calcination

The next highest calcination temperature explored was that of the center-point, 575°F/300°C. Elemental line scans shown in Figures 14A and 14B indicate that base metal fixation at this temperature was comparable to the control of Example 2.
Example 5 - Experiment No. 8 - High Temperature On-Line Calcination

In addition, the high temperature case, 750°F/400°C, demonstrated base metal fixation comparable to control samples (Example 2) - see Figures 15A and 15B.

The conclusion drawn from the line scan data is that a minimum calcination temperature of 575°F/300°C is exemplary for decomposition and preventing base metal migration to the top coat layer. These results support use of even higher temperatures in the present on-line process, e.g. 875°F/470°C, as was successfully applied to other catalyst design combinations, including those used with current manufacturing processes, with a fixed cycle time of 11 seconds to demonstrate process robustness, as discussed in Example 1 and summarized in Table 1.

Example 6 - Engine Testing for Catalytic Performance using Examples 3, 4, and 5

Experimental catalysts 11, 4, and 8 were aged for 100 hrs using North American GM RAT 875 protocol then tested on the Chevy Cobalt. As shown in Figure 16, all experiments performed better than the control sample and thus demonstrate improved performance characteristics for catalysts prepared using the present on-line calcination process.

Example 7 - Aged Sample Product Morphology (SEM)

In order to confirm comparable adhesion and washcoat morphology, aged samples were analyzed via SEM as shown in Figures 17A and 17B. Adhesion and washcoat morphology of the DoE sample in Fig. 9B (Experiment No. 8 of Example 5) was proven to be comparable to control in Fig. 17A. It was also noted that all DoE samples had less bottom coat accumulated in the cell corners (fillets) and more on the flats, such that the top coat layer fills in the bottom coat void created in the fillet. This is a characteristic of newly designed washcoats and is most probably a contributing factor towards improved performance.

Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments," "various embodiments," or "an embodiment" means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the invention. Thus, the appearances of the phrases such as "in one or more embodiments," "in certain embodiments," "in one embodiment" "in various embodiments," or "in an embodiment" in various places throughout this specification are not necessarily referring to the same embodiment of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

Although the invention herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It will be apparent to those skilled in the art that various modifications and variations can be made to the method and apparatus of the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present invention include modifications and variations that are within the scope of the appended claims and their equivalents.
WHAT IS CLAIMED IS:

1. An apparatus for calcining a monolithic catalytic substrate comprising:
   a substrate-receiving portion comprising an upper calciner section and a lower calciner section,
   wherein the upper calciner section and the lower calciner section are configured and dimensioned to fit over
   a catalytic substrate and form a fluid-tight seal when in a closed position; and
   a heating fluid source, which provides a heating fluid at an intended temperature, operatively
   associated and in fluid communication with the lower calciner section, wherein the heating fluid is delivered
   to an inlet end of the lower calciner section.

2. The apparatus of claim 1, which further comprises a heating fluid pump operatively
   associated and in fluid communication with the heating fluid source to propel the heating fluid through the
   heating fluid source where the temperature of the heating fluid is increased to an intended temperature.

3. The apparatus of claim 2, wherein the heating fluid is a gas and the heating fluid pump is a
   blower or compressor that produces a heating fluid volumetric flow rate in the range of about 50 scfm to
   about 150 scfm.

4. The apparatus of claim 2, wherein the heating fluid source is a hot air combustion system
   comprising a combustion chamber and a gas burner that increases the temperature of the heating fluid to the
   intended temperature in the range of about 350°C to about 550°C.

5. The apparatus of claim 2, wherein the heating fluid source is a heat exchanger that increases
   the temperature of the heating fluid to the intended temperature in the range of about 350°C to about 550°C.

6. The apparatus of claim 1, which further comprises a transfer duct operatively associated and
   in fluid communication with the heating fluid source and the lower calciner section, wherein the transfer
   duct forms a fluid path between the heating fluid source and the lower calciner section;
   a water reservoir for providing a quantity of deionized water for injection into the entry duct;
   an injection nozzle projecting into the entry duct; and
   a water pump operatively associated with the water reservoir and the injection nozzle that propels
   the water from the reservoir through the injection nozzle into the entry duct for de-greening a catalytic
   substrate.

7. The apparatus of claim 6, which further comprises a safety interlock comprising a water
   pump controller and a temperature sensor operatively associated with the source duct, wherein the interlock
   prevents the water pump from operating and shuts the water pump off if the temperature of the entry duct
   detected by the temperature sensor is below the intended operating temperature.
8. The apparatus of claim 3, which further comprises:
   an exhaust duct operatively associated and in fluid communication with the upper calciner section to evacuate the heating fluid.

9. The apparatus of claim 1, which further comprises:
   a by-pass duct connected to and in fluid communication with the source duct;
   a bypass control valve inserted into and operatively associated with the by-pass duct; and
   a calcining control valve inserted into and operatively associated with the source duct down-stream of the by-pass duct, wherein the calcining control valve and the bypass control valve function in tandem to redirect the heating fluid from the lower calciner section to the by-pass duct.

10. The apparatus of claim 9, which further comprises:
   an inlet pressure transducer operatively associated with the lower calciner section, which generates an inlet pressure value of the heating fluid entering the lower calciner section;
   an outlet pressure transducer operatively associated with the upper calciner section, which generates an outlet pressure value of the heating fluid exiting the upper calciner section; and
   a differential pressure controller in electrical communication with the inlet pressure transducer and outlet pressure transducer that calculates the pressure difference between the outlet pressure value and the inlet pressure value, and adjusts the heating fluid pump to propel more or less heating fluid through the heating fluid source depending on the pressure difference.

11. The apparatus of claim 9, wherein the heating fluid is diverted to the exhaust duct by closing the calcining control valve and opening the bypass valve in tandem when the upper calciner section and the lower calciner section are not in a closed position.

12. A method of calcining a catalytic substrate, comprising:
   positioning a catalytic substrate comprising a plurality of longitudinal cells between a lower calciner section and an upper calciner section;
   moving the upper calciner section and/or lower calciner section linearly to encase the catalytic substrate within the upper calciner section and lower calciner section, wherein a fluid-tight seal is formed by the upper calciner section and the lower calciner section around the catalytic substrate such that a heating fluid delivered to an inlet end of the lower calciner section passes through the plurality of longitudinal cells of the catalytic substrate; and
   delivering a heating fluid at an intended temperature to an inlet end of the lower calciner section.
13. The method of claim 12, wherein the heating fluid is delivered to the inlet end of the lower calciner section at a volumetric flow rate in the range of about 50 scfm to about 150 scfm.

14. The method of claim 12, which further comprises:
5 propelling the heating fluid with a heating fluid pump at an intended volumetric flow rate to a heating fluid source operatively associated with the heating fluid pump;
heating the heating fluid up to an intended temperature within the heating fluid source prior to delivering the heating fluid at the intended temperature to an inlet end of the lower calciner section.

15. The method of claim 14, wherein the heating fluid is heated to the intended temperature in the range of about 350°C to about 550°C.

16. The method of claim 14, which further comprises:
conveying the heating fluid from the heating fluid source to the inlet end of the lower calciner section through a delivery duct; and
injecting a spray of water into the delivery duct if the heating fluid being conveyed through the transfer duct is at the intended temperature.

17. The method of claim 16, wherein the intended temperature of the heating fluid being conveyed through the transfer duct is in the range of about 450°C to about 550°C.

18. A system for preparing a catalytic substrate, comprising:
a first catalytic substrate coating station that applies at least one washcoat comprising a catalytic slurry and a liquid carrier to at least a portion of the catalytic substrate;
at least one drying station that removes at least a portion of the liquid carries from the at least a portion of the catalytic substrate;
one or more calcining stations comprising an upper calciner section and a lower calciner section, wherein the upper calciner section and the lower calciner section are configured and dimensioned to fit over the catalytic substrate and form a fluid-tight seal, and a heating fluid source that supplies a volume of heating fluid at an intended temperature operatively associated with the lower calciner section, wherein the heating fluid is delivered to an inlet end of the lower calciner section to calcine the catalytic slurry of the washcoat to the cell walls of the catalytic substrate; and
a substrate gripper that holds the catalytic substrate and transfers the catalytic substrate between the catalytic substrate coating station, the at least one drying station, and the one or more calcining stations,
wherein one calcining station of the one or more calcining stations is adjacent to one of the at least one drying stations.
19. The system of claim 18, wherein the substrate gripper comprises a silicone rubber insert that can operate continuously at 600°F.

20. The system of claim 18, which further comprises:

- a second catalytic substrate coating station that applies at least one additional washcoat comprising a catalytic slurry and a liquid carrier to at least a portion of the catalytic substrate after the catalytic substrate has been calcined at least once at the one or more calcining stations; and
- at least one weighing station that measures the weight of the catalytic substrate, wherein the substrate gripper transfers the catalytic substrate from the catalytic substrate coating station, the drying station, or the calcining station to the at least one weighing station to determine a wet and/or a dry weight of the catalytic substrate.
FIG. 7

710: Bring Heating Fluid Pump to 10%-20% of output

720: Ignite Fuel in Combustion Chamber

730: Open Bypass Valve and Close Control Valve

740: Increase Heating Fluid Pump to 100% of Output

780: Pass Heating Fluid at Intended Temperature through Catalytic Substrate

785: Provide Feedback Control to Heating Fluid Pump to Achieve ΔP Across Catalytic Substrate

770: Turn On Water Pump to Inject Water into the Entry Duct

790: Close Control Valve and open Bypass Valve to Redirect Heating Fluid to Exhaust

799: Open Upper Calciner and Lower Calciner Sections to Remove Catalytic Substrate

750: Position Catalytic Substrate between Upper Calciner Section and Lower Calciner Section

760: Close Upper Calciner Section and Lower Calciner Section around Catalytic Substrate
TEX-0311H1 Single Coat as "Standard" Case

Low % Decomposition, Round Contour, Standard Length 4.66" x 5.0" L 400/4

Temperature (°F)

Time (s)

FIG. 10
FIG. 12B

Experiment 11 inlet (225/350/400/4000)

Sr, Ba, La, Pd

Pd

microns

Sr, Ba, La

0 18 36 54 72 90 108 126 144
Experiment 4 (225/350/350/575)

FIG. 13A
A. CLASSIFICATION OF SUBJECT MATTER
B01J 6/00(2006.01)i, B01J 37/08(2006.01)i

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)
B01J 6/00; B01J 8/02; B05C 3/00; C23C 13/08; B05D 3/12; B01J 19/00; C04B 14/10; B05C 13/00; B01J 37/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: Calcination, apparatus, monolithic catalytic substrate, heating fluid, calincer, coating

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "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)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

*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

*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

"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

"&" document member of the same patent family

Date of the actual completion of the international search: 23 June 2016 (23.06.2016)
Date of mailing of the international search report: 24 June 2016 (24.06.2016)

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Form PCT/ISA /210 (second sheet) (January 2015)
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