METHOD OF COATING A MONOLITH SUBSTRATE WITH CATALYST COMPONENT

The present invention relates to a method of, and an apparatus for, coating a honeycomb monolith substrate comprising a plurality of channels with a liquid comprising a catalyst component.

"Honeycomb monolith substrate" as defined herein includes metal and ceramic flow-through monoliths having a plurality of channels or cells which extend longitudinally along the length of the substrate structure and wherein the channels are open at both ends thereof; and metal and ceramic filters including ceramic wall-flow filters having a plurality of channels or cells which extend longitudinally along the length of the substrate structure and wherein channels at a first end of the substrate that are open are blocked at the opposite end and channels that are open at the opposite end are blocked at the first end, the arrangement being such that every other adjacent cell has an open end (or a blocked end) on the first end of the wall-flow filter and a blocked end (or an open end) on the opposite end thereof so that when an end of the wall-flow filter is viewed it resembles a chess board of open and blocked channels. Fluid communication between the open channels at the first end of the wall-flow filter and the open channels of the opposite end thereof is via the porous wall structure of the wall-flow filter.

The definition "honeycomb monolith substrate" also includes metallic so-called "partial filters" such as that which is disclosed in WO 01/80978 or the substrate disclosed in EP 1057519.

Typically, ~~ceramic~~ materials for manufacturing honeycomb monolith substrates include sintered metal or ceramic materials, such as silicon carbide, aluminium nitride, silicon nitride, aluminium titanate, ~~sintered metal,~~ alumina, cordierite, mullite, pollucite, a thermet such as Al_2O_3/Fe, Al_2O_3/Ni or B_4C/Fe, or composites comprising segments of any two or more thereof.

The formulation of liquids comprising catalyst components for coating honeycomb monolith substrates are known to those skilled in the art and include: aqueous solutions of platinum group metal compounds, such as platinum, palladium and rhodium compounds, aqueous solutions of alkali metal and alkaline earth metal compounds for depositing compounds for absorbing NO_x on the substrates, and other

shorter axial length of a part to the same washcoat loading will be less than for a longer axial length of a part.

The vacuum to be applied will generally be in the order of -5kpa to -50kpa, with durations ranging from about 0.3 seconds to about 2 seconds, depending on the washcoat solids content (longer vacuum duration for lower washcoat solids content) and size of the part (larger volume parts requiring longer duration and higher vacuum application). However, typically vacuum applications can be of the order of about 1 second. Larger substrates, e.g. those intended for heavy-duty Diesel vehicles, may require higher vacuum application, such as minus 40-50kpa.~~, whereas light-duty Diesel vehicle parts may require vacuum application of the~~

The inventors have found that a better coating profile can be achieved by applying a vacuum at step (v) following inversion of the part in at least two steps: a first short, relatively weak vacuum application (of the order of -5 to -10 kpa) at relatively low vacuum pressure and without application of any holding means such as inflatable collars in the vacuum means; followed by a second longer and stronger vacuum with holding means actuation. It is believed that the shorter vacuum application serves to clear the piston surface and allow the washcoat to run along the length of the channels before the second, higher vacuum withdraws the liquid washcoat component thus immobilising the washcoat solids on a surface of the part. The time between the first and second vacuum applications may be from 5-10 seconds, such as 6-8 seconds. Heavy-duty Diesel vehicle parts may require a third or subsequent vacuum application.

The inventors have found that the methods of the invention have particular application for making wallflow filters comprising catalysts for catalysing the selective reduction of oxides of nitrogen with nitrogenous reductants such as ammonia and ammonia precursors, such as urea, for vehicular use. Such selective catalytic reduction (SCR) catalysts include $V_2O_5/WO_3/TiO_2$ and transition metal-exchanged zeolites such as Fe/Beta zeolite or Cu/CHA. A particular difficulty with making such products is balancing the competing requirements of retaining catalyst activity at an acceptable backpressure. High backpressure has a negative impact on power output and fuel economy. As emission standards, i.e. the quantities of pollutants it is permissible to emit from a vehicle, e.g. Euro 5 and Euro 6, become ever tighter they are also including legislated requirements for in-use on-board diagnostic (OBD) verification of continuing

According to a further aspect, the invention provides a method of coating outlet channels of a wallflow filter substrate monolith to which the manufacturer of the wallflow filter substrate monolith has pre-coated to inlet channels thereof a surface membrane layer comprising finely divided inorganic solids with an axially substantially uniform catalyst washcoat., ~~which method comprising the steps of~~

Advantages of this aspect of the present invention include that catalyst washcoating (via the outlet channels) decreases the coating gradient and gives lower soot loaded backpressure, (where ammonia or an ammonia precursor is used as a reductant) a higher NH_3 storage and a higher NO_x conversion (fresh and hydrothermally aged) compared to an identical catalysed substrate monolith wherein the catalyst washcoat is instead applied to the outlet channels by a conventional dip-coating technique (as described in WO '497. The inventors believe that this improved coating uniformity should also contribute to better flow distribution over the filter, which is relevant for dosing of reducing agents such as nitrogenous reducing agents and subsequent control of NH_3 slip and NO_x conversion.

As can be seen in Example 1 and Figure 8, reducing the amount of catalyst on the rear of a filter is also beneficial for "real-world" ageing conditions, as this region is generally exposed to more severe conditions (higher temperatures and greater ash exposure) which can result in relatively lower catalytic performance from this region than that of the front part of the filter. Utilising the coating method according to the present invention (via the outlet channels instead of dip coating via the outlet channels) can decrease the proportion of the catalyst coated on the rear of the filter and should give a real-world performance benefit.

A further advantage of the methods of the present invention generally over conventional dip-coating methods is that selective adsorption of components from a multi-component catalyst washcoat at the expense of one or more other components of the washcoat by the honeycomb substrate monolith can be substantially reduced or eliminated compared to a conventional dip coating method.

~~According to a further aspect, the invention provides a catalysed wallflow filter substrate monolith to which the manufacturer of the wallflow filter substrate monolith has pre-coated to inlet channels thereof a surface membrane layer comprising finely divided refractory solids, wherein the outlet channels comprise an axially substantially uniform coating~~

~~profile of catalyst washcoat, which catalysed wallflow filter substrate monolith is obtainable by the method according to the invention.~~

~~According to a further aspect, the invention provides a catalysed wallflow filter substrate monolith to which the manufacturer of the wallflow filter substrate monolith has pre-coated to inlet channels thereof a surface membrane layer comprising finely divided refractory solids , wherein the outlet channels comprise an axially substantially uniform coating profile of catalyst washcoat, wherein the washcoat loading in an axially upstream half of the catalysed wallflow filter substrate monolith is with 10% of the washcoat loading in the axially downstream half thereof.~~

~~In embodiments, the porosity of the wallflow filter substrate monolith according to the latter two aspects of the invention prior to coating is from 40 to 80%. In preferred embodiments, the porosity of filters for use in the present invention are typically >40% or >50% and porosities of 45-75% such as 50-65% or 55-60%.~~

~~In further embodiments, a mean pore volume of the wallflow filter substrate monolith prior to coating is from 8 to 45μm, for example 8 to 25μm, 10 to 20μm or 10 to 15μm. In particular embodiments, the first mean pore size is >18μm such as from 15 to 45μm, 20 to 45μm e.g. 20 to 30μm, or 25 to 45μm.~~

In embodiments, the catalyst washcoat applied to the outlet channels of the wallflow filter substrate monolith ~~of the invention~~ is a NO_x trap, a catalysed soot filter washcoat comprising supported platinum group metal or a NH_3-SCR catalyst, preferably a NH_3-SCR catalyst.

Preferably the NH_3-SCR catalyst comprises a transition metal exchanged zeolite and most preferably the transition metal is selected from the group consisting of copper, iron, cerium and mixtures of any two or more thereof and the zeolite is selected from the group consisting of Ferrierite, CHA, BEA and MFI (ZSM-5). Particularly preferred combinations are Cu/CHA, Fe/Ferrierite, Fe/ or Fe-Ce/ZSM-5 and Fe or Fe-Ce/BEA.

In order that the invention may be more fully understood, reference will now be made to the series of schematic representations of an embodiment of the apparatus and method steps of the invention shown in the accompanying drawings, in which:

nozzle, which nozzle is housed in a container, which container comprising a gas inlet and a gas outlet, said gas outlet connecting with a conduit for transporting gas from the gas outlet to atmosphere, means for detecting a rate of gas flowing through the gas inlet and means for forcing an oxidising gas to flow from the gas inlet via the container, the gas outlet and the conduit to atmosphere, a station for collecting particulate matter from gas flowing through the conduit and means for controlling the gas flow-forcing means in response to a detected gas flow rate at the gas inlet, whereby the rate of gas flow at the gas inlet is maintained at a desired rate to provide sub-stoichiometric fuel combustion within the container, thereby to promote particulate matter formation.

The filters were fitted each in turn in the station with the inlet channels pre-coated by the supplier with membrane layer disposed to receive particulate-containing exhaust gas first. The apparatus was operated with standard forecourt pump Diesel fuel containing a maximum of 50 ppm sulphur. The DPG unit was operated with a gas mass flow rate of 250 kg/hour, a particulate generation rate of 10 g/hr with an inline particulate silicon carbide filter maintained at about 240°C. During the particulate matter loading of each filter the back pressure was determined by a differential pressure sensor and logged on a computer every 10 seconds.

The results are shown in Figure 9.~~, from which it can be seen that the~~

EXAMPLE 5 – Fresh and Aged Bench Engine Activity Comparison of Coated Filters

The filters of Example 1 and Comparative Example 2 were each fitted in turn to the exhaust gas system of a bench-mounted Euro IV compliant, 2 litre direct injection, common rail engine (suitable e.g. for a passenger car) downstream of a 1 litre oxidation catalyst (95 g/ft^3 with 2:1 weight ratio of platinum and palladium coated onto a 350 cell per square inch cordierite monolithic flow-through substrate), with the filter orientated so that the channels provided with the pre-coated membrane layer were on the gas inlet side of the filter. Standard Diesel fuel was used with 50 ppm sulphur content. A urea injector for injecting urea solution (AdBlue) into exhaust gas was disposed between the oxidation catalyst and the filter. Diesel fuel of <10ppm sulphur was used. Following an initial warm-up phase, the engine was run at a series of engine loads in order to achieve a desired filter inlet temperature. The test conditions used were as shown in Table 1. "Alpha" is defined as the NH_3/NO_x ratio. So for an "Alpha of 0.7, a theoretic maximum

13. Apparatus according to claim 12, wherein the housing, piston and cylinder are inverted by the inverting means.

14. Apparatus according to any of claims 5 to 13, comprising means for sealing an outer surface of the substrate from the open ends of the channels at the lower end of the substrate.

15. Apparatus according to claim 14 wherein the holding means comprises a housing for receiving at least the lower end of the substrate, and an inflatable collar disposed on an internal surface of the housing for engaging with an outer surface of the substrate ~~when appendant to claim 7~~, and wherein the means for sealing the outer surface of the substrate from the opens ends of the channels at a lower end of the substrate comprises the inflatable collar.

16. Apparatus according to any of claims 5 to 15, wherein the vacuum means comprises a funnel, the wider end of which is for receiving the inverted end of the substrate.

17. Apparatus according to any of claims 5 to 16, comprising computer operated means for controlling the apparatus to perform the method steps of any of claims 1 to 4.

~~18. A catalysed wallflow filter substrate monolith to which the manufacturer of the wallflow filter substrate monolith has pre-coated to inlet channels thereof a surface membrane layer comprising finely divided refractory solids, wherein the outlet channels comprise an axially substantially uniform coating profile of catalyst washcoat, which catalysed wallflow filter substrate monolith is obtainable by the method of any of claims 1 to 4.~~

~~19. A catalysed wallflow filter substrate monolith to which the manufacturer of the wallflow filter substrate monolith has pre-coated to inlet channels thereof a surface membrane layer comprising finely divided refractory solids , wherein the outlet channels comprise an axially substantially uniform coating profile of catalyst washcoat, wherein the washcoat loading in an axially upstream half of the catalysed wallflow filter substrate monolith is with 10% of the washcoat loading in the axially downstream half thereof.~~

20. A catalysed wallflow filter substrate monolith according to claim 18 or 19, wherein the porosity of the wallflow filter substrate monolith prior to coating is from 40 to 80%.

21. A catalysed wallflow filter substrate monolith according to claim 18, 19 or 20, wherein a mean pore volume of the wallflow filter substrate monolith prior to coating is from 8 to 45μm.

22. A catalysed wallflow filter substrate monolith according to claim 18, 19, 20 or 21, wherein the catalyst washcoat is a NO_x trap, a catalysed soot filter washcoat comprising supported platinum group metal or a NH_3-SCR catalyst.

23. A catalysed wallflow filter substrate monolith according to claim 22, wherein the NH_3-SCR catalyst comprises a transition metal exchanged zeolite.

24. A catalysed wallflow filter substrate monolith according to claim 23, wherein the transition metal is selected from the group consisting of copper, iron, cerium and mixtures of any two or more thereof and the zeolite is selected from the group consisting of Ferrierite, CHA, BEA and MFI (ZSM-5).