(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 February 2023 (23.02.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/021287 A1

(51) International Patent Classification:
B01D 53/94 (2006.01) *B01J 37/00* (2006.01)
B01J 23/56 (2006.01)

(21) International Application Number:
PCT/GB2022/052133

(22) International Filing Date:
17 August 2022 (17.08.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/260,465 20 August 2021 (20.08.2021) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

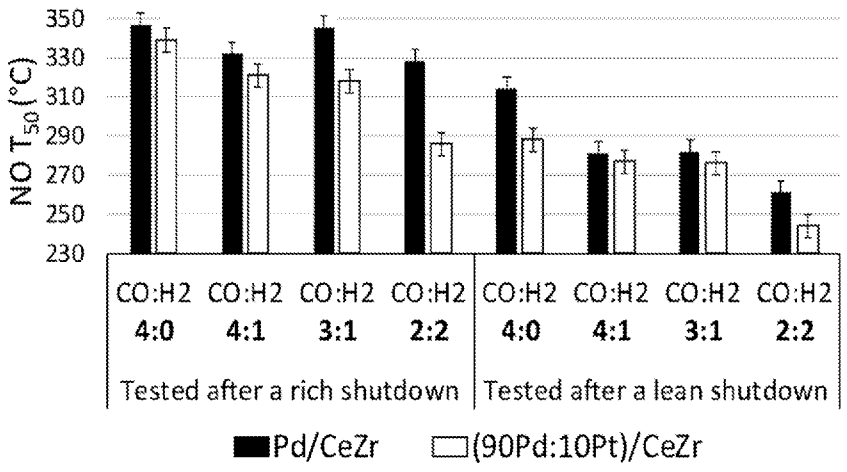
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) Title: IMPROVED TWC CATALYSTS FOR GASOLINE ENGINE EXHAUST GAS TREATMENTS

FIG. 4



(57) Abstract: A catalyst composition comprising a first platinum group metal (PGM) component and a first support material, wherein the first PGM component comprises platinum (Pt) and palladium (Pd) and is supported on the first support material; and wherein the first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5.

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IMPROVED TWC CATALYSTS FOR GASOLINE ENGINE EXHAUST GAS TREATMENTS

FIELD OF THE INVENTION

The present invention relates to a catalysed article useful in treating exhaust gas emissions from gasoline engines and specifically to a catalyst composition, a catalyst article, an emission treatment system, a method of treating an exhaust gas and a method of manufacturing a catalyst article.

BACKGROUND OF THE INVENTION

Internal combustion engines produce exhaust gases containing a variety of pollutants, including hydrocarbons (HCs), carbon monoxide (CO), and nitrogen oxides ("NO_x"). Emission control systems, including exhaust gas catalytic conversion catalysts, are widely utilized to reduce the amount of these pollutants emitted to atmosphere. A commonly used catalyst for gasoline engine exhaust treatments is the TWC (three way catalyst). TWCs perform three main functions: (1) oxidation of CO; (2) oxidation of unburnt HCs; and (3) reduction of NO_x.

Palladium (Pd) and rhodium (Rh) have been widely used in TWC formulations to reduce harmful emissions in gasoline vehicles. In fact, at present TWC technology is highly dependent on Pd/Rh systems. However, in recent years, these precious metal prices have climbed up to be even more precious, due to rising demand in the market. On the other hand, tighter and tighter environmental regulations worldwide have forced automobile industries to put even more precious metals into their catalytic converters. As a result, there is a potential market risk due to the recent Pd demand outweighing the Pd supply.

In the meantime, platinum (Pt) has become a more attractive candidate for gasoline applications due to its relatively cheaper price. In the last 12 months (from July 2021, according to http://www.platinum.matthey.com), the average prices of Pt and Pd were about $1085 and $2660 dollars / Oz respectively. Thus, there are huge financial incentives on how to introduce Pt into catalyst formulations, to at least partially replace Pd while hoping to maintain comparable catalyst performances.

Thus, there is a desire to provide a cheaper catalyst for TWC applications that may still have comparable or improved activity compared to the conventional TWC catalysts currently in use.

SUMMARY OF THE INVENTION

One aspect of the present disclosure is directed to a catalyst composition comprising a first platinum group metal (PGM) component and a first support material, wherein the first PGM component comprises platinum (Pt) and palladium (Pd) and is supported on the first support material; and wherein the first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5.

Another aspect of the present disclosure is directed to a catalyst article for treating exhaust gas comprising: a substrate; and a first catalytic region comprising a first platinum group metal (PGM) component and a first support material, wherein the first PGM component comprises platinum (Pt) and palladium (Pd) and is supported on the first support material; and wherein the first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5.

The invention also encompasses an emission treatment system comprising the catalyst composition or catalyst article described herein.

Another aspect of the present disclosure is directed to a method of treating an exhaust gas, the method comprising: providing the catalyst composition or the catalyst article described herein; and contacting the catalyst composition or catalyst article with an exhaust gas.

Another aspect of the present disclosure is directed to a method of manufacturing a catalyst article, the method comprising: providing a slurry comprising: platinum (Pt) and palladium (Pd) ions in a molar ratio of from about 5:95 to about 95:5, and a support material; disposing the slurry on a substrate; and heating the slurry to form nanoparticles of the Pt and Pd on the support material.

The invention also encompasses a catalyst article as described herein, wherein the catalyst article is obtained or obtainable by the method of manufacturing a catalyst article described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a shows one embodiment according to the present invention, the first catalytic region extends 100% of the axial length L, as top layer; the second catalytic region extends 100% of the axial length L, as bottom layer.

FIG. 1b depicts a variation of **FIG. 1a**.

FIG. 2a shows one embodiment according to the present invention, the first catalytic region extends less than 100% of the axial length L, from the inlet end; the second catalytic region extends less than 100% of the axial length L, from the outlet end. The total length of the second and the first catalytic region is equal or less than the axial length L.

FIG. 2b depicts a variation of **FIG. 2a**.

FIG. 2c shows one embodiment according to the present invention, the first catalytic region extends less than 100% of the axial length L, from the inlet end; the second catalytic region extends less than 100% of the axial length L, from the outlet end. The total length of the second and the first catalytic region is greater than the axial length L.

FIG. 2d depicts a variation of **FIG. 2c**.

FIGS. 3a and **3b** show light-off temperature results from Example 1.

FIG. 4 show light-off temperature results for different $CO:H_2$ ratios in Example 1.

FIGS. 5a-5c show emissions results for Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention seeks to tackle at least some of the problems associated with the prior art or at least to provide a commercially acceptable alternative solution thereto.

In a first aspect, the present invention provides a catalyst composition comprising a first platinum group metal (PGM) component and a first support material, wherein the first PGM component comprises platinum (Pt) and palladium (Pd) and is supported on the first

support material; and wherein the first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5.

Each aspect or embodiment as defined herein may be combined with any other aspect(s) or embodiment(s) unless clearly indicated to the contrary. In particular, any features indicated as being preferred or advantageous may be combined with any other feature indicated as being preferred or advantageous.

Surprisingly, when used in an emission treatment system, the catalyst composition of the present invention provides comparable or improved catalytic (i.e. TWC) activity compared to conventional catalyst compositions comprising Pd with no Pt replacement. For a wide range of TWC operating conditions, Pt is known to have lower catalytic (i.e. TWC) activity compared to Pd. Thus, it is surprising that replacing any amount of the Pd in the catalyst composition with Pt would not have a negative effect on the catalytic activity thereof. However, the inventors have surprisingly found that replacing from about 5 mol.% to about 95 mol.% of the Pd in such a catalyst composition with Pt (i.e. in order to provide a desirably cheaper catalyst composition) provides a catalyst composition with comparable or even improved catalytic (i.e. TWC) activity. As described in more detail herein, at certain specific ratios of Pt to Pd (i.e. replacing a certain amount of Pd with Pt within the above range), a catalyst composition can be obtained that may actually have improved catalytic (i.e. TWC) activity compared to catalyst compositions comprising Pd with no Pt replacement. Such catalyst compositions may also demonstrate lower light-off temperatures compared to catalyst compositions comprising Pd with no Pt replacement.

Moreover, it has also surprisingly been found that such a catalyst composition may be more robust to changes in exhaust gas conditions, for example from lean to rich conditions and in different ageing conditions. Along with increased catalytic (i.e. TWC) activity, this may be a particularly advantageous property for use in exhaust systems commonly used at present.

In particular, when used in an exhaust system the catalyst composition of the present invention may surprisingly result in a significantly improved reduction in CO emissions, improved NOx conversion and comparable or improved reduction in hydrocarbon (HC) emissions in combination. Thus, not only may the catalyst composition described herein be

desirably cheaper than conventionally used catalyst compositions comprising Pd with no Pt replacement, but such catalyst compositions may also exhibit desirably improved catalytic performance. Without wishing to be bound by theory, it is hypothesised that the increased performance against CO emissions may be as a result of the Pd being less poisoned by CO or having better CO oxidation activity due to the presence of the Pt and interaction thereof with the Pd.

Without wishing to be bound by theory, it is also hypothesised that a Pt-Pd alloy may form in the catalyst composition, in which the alloy substantially maintains the Pd character (for example due to comprising a majority of Pd). It is thought that this may contribute to the increased or comparable performance that may be provided by the catalyst composition described herein. In other words, the maintenance of the Pd character of such an alloy may mean that the replacement of Pd with the less-active Pt would not reduce the catalytic (i.e. TWC) activity of the catalyst composition. For example, the presence of Pt may induce an electronic modification of the Pd such that the adsorption/dissociation energies of the pollutants on the metal are altered, while still maintaining substantially Pd character. This may then lead to the above-described advantageous properties, without wishing to be bound by theory.

The term "catalyst composition" as used herein may encompass a composition that exhibits catalytic activity, particularly for use in the treatment of exhaust gas, preferably from a gasoline engine. In other words, the catalytic composition may demonstrate catalytic activity towards one or more of the oxidation of CO, the oxidation of unburnt HCs and the reduction of NOx. Preferably, the catalyst composition is for three-way catalysis. In other words, the catalyst composition may be a three-way catalyst.

Unless otherwise specified, the terms "first", "second", "third" etc. as used herein are for the purposes of clarity only and are used as labels to help distinguish certain features from one another. This wording is not intended to limit any particular order of features or components, for example, or indicate whether a certain feature is preferred over another.

The term "platinum group metal (PGM)" as used herein may encompass a metal selected from the group consisting of Ru, Rh, Pd, Os, Ir and Pt, preferably a metal selected

from the group consisting of Ru, Rh, Pd, Ir and Pt. In general, the term "PGM" preferably refers to a metal selected from the group consisting of Rh, Pt and Pd.

The first PGM component comprises Pt and Pd. Preferably, the first PGM component consists essentially of, or even consists of Pt and Pd. The first catalyst component may comprise PGMs other than Pt and Pd in addition to Pt and Pd.

The expression "consist essentially" as used herein limits the scope of a feature to include the specified materials or steps, and any other materials or steps that do not materially affect the basic characteristics of that feature, such as for example minor impurities. The expression "consist essentially of" embraces the expression "consisting of".

The term "support material" as used herein may encompass any material that is capable of supporting the first PGM component thereon or therein. The support material may take any form, but is typically in the form of a powder, more typically a high surface area powder. When the catalyst composition of the present invention is used to prepare a catalysed filter, such as a wall flow filter or flow-through filter, for example, the support material will typically be in the form of a powder having a D_{50} of, for example, from 0.1 to 30 μm, more typically from 0.5 to 25 μm as measured using TEM, even more typically 1 to 20 μm. Such particle sizes may facilitate desirable rheological properties of a slurry used to coat the filter. The support material may function as a washcoat. The support material may be a washcoat or may be part of a washcoat.

The support material may also serve as an oxygen storage material, which stores and releases oxygen respectively at fuel lean and fuel rich conditions, for facilitating the three-way catalytic conversion.

The first PGM component is supported on the first support material. The term "supported on" as used in this context may encompass a situation where the first PGM component is loaded on the external surface of the support material (e.g. on the surface of a high-surface area metal oxide support material) or contained within the support material, such as within the pores thereof (e.g. within the pores of a zeolite support material).

The first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5. In other words, the first PGM component has from about 5 to about 50 mol.% Pt, based on the total moles of Pt and Pd. When the first PGM component consists of Pt and Pd, the first PGM component therefore comprises about 5 to about 50 mol.% Pt, based on the total moles of the first PGM component.

The Pt:Pd molar ratio is preferably from about 5:95 to about 90:10, more preferably from about 5:95 to about 75:25, even more preferably from about 10:90 to about 50:50, still even more preferably from about 10:90 to about 35:65, and most preferably from about 10:90 to about 25:75; for example preferably any of from about 7:93 to about 15:85, from about 7:93 to about 14:86, from about 7:93 to about 13:87, from about 7:93 to about 12:88, from about 7:93 to about 11:89, from about 8:92 to about 15:85, from about 8:92 to about 14:86, from about 8:92 to about 13:87, from about 8:92 to about 12:88, from about 8:92 to about 11:89, from about 9:91 to about 14:86, or from about 9:91 to about 13:87. In some preferred embodiments, the Pt:Pd molar ratio may be from about 9:91 to about 11:89.

The inventors have surprisingly found that replacing approaching about 10 mol.% Pd with Pt in a Pd-containing catalyst, such as a TWC catalyst, may provide improved catalytic performance as described herein, while also providing for a cheaper catalyst composition due to the current difference in price between Pt and Pd. As demonstrated in the Examples below, the best advantages have been shown when the Pt:Pd molar ratio is approaching about 10:90. However, throughout the claimed range (for example, approaching a Pt:Pd molar ratio of 95:5) a cheaper catalyst may still be provided which may unexpectedly provide at least comparable, but preferably improved catalytic (i.e. TWC) performance.

The Pt and Pd are preferably at least partially alloyed, more preferably substantially alloyed, even more preferably completely alloyed. The term “alloy” or “alloyed” as used herein takes on its usual meaning in the art. TEM and XRD characterisation techniques may be used to help determine whether or not a Pt-Pd alloy has formed, using techniques known to the skilled person. Without wishing to be bound by theory, it is hypothesised that the formation of such an alloy may contribute to the achievement of the advantageous properties, such as comparable or improved catalytic activity, lower light-off temperatures and resistance to

ageing described and demonstrated herein. Such an alloy of the Pt and Pd may form during the manufacture of the catalyst composition, such as during a calcining and/or heating step that may be performed. Alternatively, such an alloy may form during use (e.g. ageing) of the catalyst composition, due to the high temperatures experienced in exhaust systems, for example. That is, a mixture of Pt and Pd nanoparticles that may be in close proximity on the support material may coalesce and form an alloy at such temperatures, for example.

The expression "substantially alloyed" as used herein refers to at least 75% of the PGM contained within the catalytic region of interest being present as an alloyed phase. The expression "partially alloyed" as used herein refers to at least 25% of the PGM contained within the catalytic region of interest being present as an alloyed phase

The likelihood of such potentially beneficial alloying occurring may be increased during manufacture of the catalyst composition by, for example, using a method that helps to ensure a homogeneous distribution of Pt and Pd on the support material, preferably one that also ensures a homogeneous distribution of Pt and Pd nanoparticles having a small particle size on the support material, such as less than 50 nm, less than 30 nm or even less than 20 nm, in terms of the mean particle size determined by TEM. In other words, close proximity of small Pt and Pd nanoparticles on the support material may help to increase the likelihood of alloying of the Pt and Pd in the first PGM component. The first PGM component preferably consists of an alloy of Pt and Pd.

The first support material preferably comprises an inorganic oxide. The inorganic oxide is preferably selected from one or more of cerium oxide, a ceria-zirconia mixed oxide, an alumina-ceria-zirconia mixed oxide, alumina, magnesia, silica, lanthanum, neodymium, praseodymium, yttrium oxides, and mixed oxides or composite oxides thereof, or a zeolite. The inorganic oxide is preferably a metal oxide. The first support material is preferably selected from alumina, preferably gamma-alumina, a ceria-zirconia mixed oxide, or a combination thereof. In other words, the first PGM component is preferably supported on alumina and/or ceria-zirconia. Any number of support materials may be present, provided that the Pt and the Pd of the first PGM component are both supported together thereon or therein, in order to enable an interaction between the Pt and the Pd.

The alumina and/or ceria-zirconia mixed oxide is preferably doped. The alumina and/or ceria-zirconia mixed oxide is preferably doped with an oxide of one or more of lanthanum, neodymium, yttrium, niobium, praseodymium, hafnium, molybdenum, titanium, vanadium, zinc, cadmium, manganese, iron, copper, calcium, barium, strontium, caesium, magnesium, potassium and sodium, preferably one or more of lanthanum, neodymium, praseodymium and yttrium, more preferably lanthanum. Such doped oxides are particularly effective as support materials. Preferably, the dopant is present in the alumina and/or ceria-zirconia mixed oxide in an amount of from 0.001 wt.% to 20 wt.%, preferably from 0.5 wt.% to 10 wt.%.

The first support material or inorganic oxide of the first support material is preferably in the form of a powder having a D_{90} of from 0.1 to 25 μm, preferably from 0.5 to 5 μm, measured by TEM.

The term "mixed oxide" as used herein generally refers to a mixture of oxides in a single phase, as is conventionally known in the art. The term "composite oxide" as used herein generally refers to a composition of oxides having more than one phase, as is conventionally known in the art.

The catalyst composition preferably further comprises a second PGM component and a second support material. The second PGM component preferably comprises rhodium (Rh), a Rh alloy, Pt, a Pt alloy, a Rh-Pt alloy or a mixture thereof. The second PGM component preferably comprises Rh. Thus, the catalyst composition is preferably a tri-metallic (i.e. Pt, Pd and Rh) catalyst composition, which is preferably a TWC. When Rh is present, for example, this may offset any (albeit slight) deterioration in performance for catalyst compositions in which a higher-percentage of Pd has been replaced by Pd, for example over about 25 mol.%. In other words, in catalyst compositions that further comprise Rh, even for higher Pt content in the first PGM component (e.g. approaching 95:5molar ratio Pt:Pd) a comparable or improved catalytic performance may be achieved even if the higher amounts of Pt may result in minimal change in catalytic performance. Moreover, such a catalyst composition may have an even lower cost first PGM component.

In a further aspect, the present invention provides a catalyst article for treating exhaust gas comprising:

a substrate; and

a first catalytic region comprising a first platinum group metal (PGM) component and a first support material, wherein the first PGM component comprises platinum (Pt) and palladium (Pd) and is supported on the first support material; and

wherein the first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5.

The term "catalyst article" used herein may encompass an article in which a catalyst is supported thereon or therein. The article may preferably take the form of, for example, a honeycomb monolith, or a filter, e.g. preferably a wall flow filter or a flow-through filter. The catalyst article may be for use in an emission treatment system, in particular an emission treatment system for a gasoline engine, preferably a stoichiometric gasoline engine. The catalyst article may be for use in three-way catalysis. In other words, the catalyst article may be a TWC.

The term "substrate" as used herein may encompass, for example, a ceramic or metallic honeycomb, or a filter block, *e.g.* preferably a wall flow filter or flow-through filter. The substrate may comprise a ceramic monolithic substrate. The substrate may vary in its material composition, size and configuration, cell shape and density, and wall thickness. Suitable substrates are known in the art.

Unless otherwise stated, the preferences, embodiments and definitions described above for the first aspect (the catalyst composition described herein) in relation the first PGM component and the first support material apply equally to the present aspect (the catalyst article).

The term "region" or "catalytic region" as used herein refers to an area on a substrate containing a catalyst, typically obtained by drying and/or calcining a washcoat. A "region" can, for example, be disposed or supported on a substrate as a "layer" or a "zone". The area or arrangement on a substrate is generally controlled during the process of applying the washcoat to the substrate. The "region" typically has distinct boundaries or edges (i.e. it is possible to distinguish one region from another region using conventional analytical techniques).

Typically, the "region" has a substantially uniform length. The reference to a "substantially uniform length" in this context refers to a length that does not deviate (e.g. the difference between the maximum and minimum length) by more than 10 %, preferably does not deviate by more than 5 %, more preferably does not deviate by more than 1 %, from its mean value.

It is preferable that each "region" has a substantially uniform composition (i.e. there is no substantial difference in the composition of the washcoat when comparing one part of the region with another part of that region). Substantially uniform composition in this context refers to a material (*e.g.*, region) where the difference in composition when comparing one part of the region with another part of the region is 5% or less, usually 2.5% or less, and most commonly 1% or less.

The term "zone" as used herein refers to a region having a length that is less than the total length of the substrate, such as $\leq$ 75 % of the total length of the substrate. A "zone" typically has a length (*i.e.* a substantially uniform length) of at least 5% (*e.g.* $\geq$ 5 %) of the total length of the substrate.

The catalyst article preferably further comprises a second catalytic region. The second catalytic region preferably comprises a second PGM component and a second support material. The second PGM component preferably comprises rhodium (Rh), a Rh alloy, Pt, a Pt alloy, a Rh-Pt alloy or a mixture thereof. The second PGM component preferably comprises Rh. Thus, the catalyst article is preferably a tri-metallic (i.e. Pt, Pd and Rh) catalyst composition, which is preferably a TWC. As in conventional TWC catalysts, the catalytic region comprising Rh is a different catalytic region to the Pd-based catalytic region (i.e. the first catalytic region described herein). When Rh is present, for example, this may offset any deterioration in performance for catalyst compositions in which a higher-percentage of Pd has been replaced by Pd, for example over about 25 mol.%. In other words, in catalyst compositions that further comprise Rh, even for higher Pt content in the first PGM component (e.g. approaching 95:5 molar ratio Pt:Pd) a comparable or improved catalytic performance may be achieved even if the higher amounts of Pt may result in minimal change in catalytic performance. Moreover, such a catalyst article would may have an even lower cost first PGM component.

The catalyst composition, the first catalytic region and/or the second catalytic may comprise additional components such as, for example, one or more of a promoter, a binder and a thickening agent.

Promoters may include, for example, a non-PGM transition metal element, a rare earth element, an alkali or alkali earth group element, and/or a combination of two or more of the above elements within the same or different groups in periodic table. The promoter may be a salt of such elements. A particularly preferred promoter is barium, with particularly preferred salts thereof being barium acetate, barium citrate and barium sulfate, or a combination thereof, more preferably barium citrate.

Binders may include, for example, an oxide material with small particle size to bind the individual insoluble particles together in washcoat slurry. The use of binders in washcoats is well known in the art.

Thickening agents may include, for example, a natural polymer with functional hydroxyl groups that interacts with insoluble particles in washcoat slurry. It serves the purpose of thickening washcoat slurry for the improvement of coating profile during washcoat coating onto substrate. It is usually burned off during washcoat calcination. Examples of specific thickening agents / rheology modifiers for washcoats include glactomanna gum, guar gum, xanthan gum, curdlan schizophyllan, scleroglucan, diutan gum, Whelan gum, hydroxymethyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose and ethyl hydroxycellulose.

Preferably, the first catalytic region and the second catalytic region form distinct layers, wherein the second catalytic region is deposited directly on the first catalytic region, *i.e.* the first catalytic region is sandwiched between the second catalytic region and the substrate (*e.g.* a filter wall). In another preferred embodiment, the first catalytic region and the second catalytic region form distinct layers, wherein the first catalytic region is deposited directly on the second catalytic region.

The first catalytic region may be supported/deposited directly on the substrate, *i.e.* the first catalytic region is in direct contact with the substrate. Alternatively, the second catalytic region may be supported/deposited directly on the substrate.

Typically, the substrate comprises a first end and a second end with an axial length L. In some preferred embodiments, the first catalytic region extends for the entire axial length L and/or the second catalytic region extends for the entire axial length L (e.g. **FIGs. 1a** and **1b**). In other preferred embodiments, the first catalytic region extends for less than the axial length L and/or the second catalytic region extends for less than the axial length L (e.g. **FIGs. 2a-d**). When the first catalytic region extends for less than the axial length L, the first catalytic region may extend from the first end or the second end. When the second catalytic region extends for less than the axial length L, the second catalytic region may extend from the first end or the second end. When the first or second catalytic region extends for less than the axial length L, the first or second catalytic region may extend for 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, or 90%, for example, of the axial length L, *e.g.* from 10% to 90%, or from 10% to 50%, or from 10% to 30%, or from 30% to 90%, or from 50% to 90%, or from 70% to 90%, or from 20% to 80%, or from 30% to 70%, or from 40% to 60%. The first and second catalytic regions may fully, at least partially, partially or not overlap. Each configuration provides certain advantages depending on the intended use of the catalyst article.

In some preferred embodiments, the first end is an inlet end and the second end is an outlet end of the catalyst article. The terms "outlet end" and "inlet end" as used herein are used in relation to the relative intended direction of exhaust flow for when the catalyst article is placed in exhaust system, for example, the intended direction of exhaust gas being from the inlet end towards the outlet end.

The first catalytic region preferably comprises from 20 g/ft^3 to 400 g/ft^3 total Pt and Pd, preferably from 30 g/ft^3 to 250 g/ft^3 or from 40 g/ft^3 to 200 g/ft^3 total Pt and Pd. The second catalytic region preferably comprises from 2 g/ft^3 to 200 g/ft^3 Rh, preferably from 5 g/ft^3 to 100 g/ft^3 Rh.

In some preferred embodiments, the first catalytic region of the catalyst article of the present aspect is the catalyst composition according to the first aspect. In other words, in some

preferred embodiments, the first catalytic region of the catalyst article of the present aspect is formed of the catalyst composition according to the first aspect

In a further aspect, the present invention provides an emission treatment system comprising the catalyst composition or catalyst article described herein.

The emission treatment system is preferably for a gasoline engine.

The gasoline engine preferably operates under stoichiometric conditions.

In a further aspect, the present invention provides a method of treating an exhaust gas, the method comprising: providing the catalyst composition or catalyst article described herein; and contacting the catalyst composition or catalyst article with an exhaust gas.

The exhaust gas is preferably from a gasoline engine. The catalyst article is particularly suitable for treating such exhaust gas. Moreover, exhaust from a gasoline engine is typically harsher, for example higher temperature, than that from a diesel engine. Therefore, the advantageous ageing properties of the catalyst articles described herein are particularly beneficial therefor. The gasoline engine preferably operates under stoichiometric conditions.

In a further aspect, the present invention provides a method of manufacturing a catalyst article, the method comprising:

providing a slurry comprising:

platinum (Pt) and palladium (Pd) ions in a molar ratio of from about 5:95 to about 95:5, and

a support material;

disposing the slurry on a substrate; and

heating the slurry to form nanoparticles of the Pt and Pd on the support material.

The term “slurry” as used herein may encompass a liquid comprising insoluble material, e.g. insoluble particles. The slurry may comprise (1) solvent; (2) soluble content, e.g. free Pt and Pd ions (i.e. outside of the support); and (3) insoluble content, e.g. supported particles. A slurry is particularly effective at disposing a material onto a substrate, in particular for maximized gas diffusion and minimized pressure drop during catalytic conversion. The slurry is typically stirred, more typically for at least 10 minutes, more typically for at least 30

minutes, even more typically for at least an hour. The slurry therefore typically comprises a loaded support material (i.e. the support material is preferably a loaded support material). The term "loaded support material" as used herein may encompass a support material that has the Pt and Pd ions loaded thereon (e.g. on the surface of a high-surface area metal oxide support material) and/or loaded therein (e.g. within the pores of a zeolite support material). The Pt and Pd ions are typically fixed to the support, for example by electrostatic forces, hydrogen bonds, coordinate bonds, covalent bonds, and/or ionic bonds. The support material is preferably the first support material described herein.

Providing a slurry typically comprises mixing a solvent, the support material and the Pt and Pd ions (e.g. from a Pt and/or Pd salt, such as Pt or Pd nitrate).

Disposing the slurry on the substrate may be carried out using techniques known in the art. Typically, the slurry may be poured into the inlet of the substrate using a specific moulding tool in a predetermined amount, thereby disposing the loaded support material on the substrate. Subsequent vacuum and drying steps may be employed during the disposition step. When the support is a filter block, the loaded support material may be disposed on the filter walls, within the filter walls (if porous) or both.

Heating the slurry is typically carried out in an oven or furnace, more typically a belt or static oven or furnace, typically in hot air at a specific flow from one direction. The heating may comprise calcination. The heating may also comprise drying. The drying and calcination steps may be continuous or sequential. For example, a separate washcoat may be applied after the substrate is already washcoated and dried with a previous washcoat. A washcoated substrate can also be dried and calcined using one continuous heating program if coating is completed. During the heating, any complex that may have formed in the slurry may at least partially, substantially or completely decompose. In other words, the ligands of such a complex, e.g. an organic compound, are at least partially, substantially or completely removed or separated from the Pt and Pd, and are removed from the final catalyst article. Particles of such separated Pt and Pd may then begin to form metal-metal and metal-oxide bonds. As a result of the heating (calcination), the substrate is typically substantially free of organic compounds, more typically completely free of organic compounds.

The term "nanoparticle" as used herein may encompass a particle having a diameter of from 0.01 nm to 100 nm as measured by TEM. The nanoparticles may be in any shape, *e.g.* a sphere, a plate, cubic, cylindrical, hexagonal or a rod, but are typically spherical.

Following the heating step, the substrate is typically cooled, more typically to room temperature. The cooling is typically carried out in air with or without cooling agent/media, typically without cooling agent.

The slurry preferably comprises one or more of glyoxime; a glyoxime derivative; salicylaldimine, and a salicylaldimine derivative. Without wishing to be bound by theory, it is thought that complexes comprising such molecules and the Pt and/or Pd may form. Such compounds have surprisingly been found to help enable even distribution of the Pt and Pd, to help achieve the advantageous properties described and demonstrated herein, for example.

The catalyst article described herein is preferably obtained or obtainable by the method of the present aspect. However, alternative methods known to the skilled person may also be used to manufacture the catalyst article described herein, although the method of the present aspect may be particularly suitable.

The invention will now be described in relation to the following non-limiting examples.

EXAMPLE 1: LIGHT OFF PERFORMANCES IN SYNTHETIC CATALYST ACTIVITY TEST

A series of Pd-Pt supported ceria-zirconia catalysts with a total 1wt% PGM loading were made by the incipient wetness technique using $Pd(NO_3)_3$ and $Pt(NO_3)_3$ precursors. After drying, they were calcined at 650 °C for 2 hours. The mol% ratios of Pd and Pt are 100:0 (Pd-only reference), 95:5, 90:10, 79:21, 65:35, 47:53 and 0:100 (Pt-only reference), shown in **Table 1** below.

Table 1: PGM loadings of Catalysts in Example 1

	Molar Ratio of Pd: Pt
Comparative Catalyst 1	100:0
Catalyst 2	95:5
Catalyst 3	90:10
Catalyst 4	79:21

Catalyst 5	65:35
Catalyst 6	47:53
Comparative Catalyst 7	0:100

Catalysts were aged according to the TWC ageing conditions in **Table 2** and were tested under a continuous gas mix with a typical TWC gas composition. Catalysts in **Table 1** were tested from 110 to 500 °C using a ramp rate of 10 °C/min. The total flow used was 5 L/min for 0.2g of catalyst mixed with 0.2g of cordierite, which was placed in a fix bed reactor. The gases used, and their concentrations are presented in **Table 3**.

Table 2: Ageing conditions for Catalysts in Example 1

	Perturbed SCAT Ageing	
	Base mix	**+ pert. line**
Lambda	0.92	1.06
Time	300 sec	300 sec
NO	1000 ppm	
H_2O	10%	
CO	0.52%	0.52%
C_3H_8	1000 ppm	
O_2	0.27%	1.06%
N_2	90%	88%
Ramp rate	5°C/min	
Temp/time	950°C/16 hours	
Flow	120 L/hour	

Table 3: Gas mix composition for the light-off experiments in Example 1

	Perturbed SCAT test

	Base mix	+ pert. line
Lambda	0.99	0.05
Time	3 sec	3 sec
NO	2200 ppm	
CO_2	14 %	
H_2O	4 %	
CO	0.73 %	1.47%
C_3H_6	660 ppm	
C_2H_6	330 ppm	
H_2	0.23 %	0.46%
O_2	Dependable on λ	1%
Ramp rate	10°C/min	
Max. Temp.	500°C	
WHSV	750 $Lg^{-1}h^{-1}$	

The results are shown in **FIGs. 3a** and **3b**, which show the light-off temperatures (T_{60}) measured for each catalyst. **FIG. 3a** shows after lean shutdown and **FIG. 3b** shows after rich shutdown ageing conditions. Catalyst 3 (with a 90:10 Pd-Pt molar ratio) performed better following both rich and lean shut-down conditions following the ageing treatment, compared to Comparative Catalysts 1 and 7.

Catalyst 3 (with a 90:10 Pd-Pt molar ratio) was then tested across 6 further TWC gas mixes whereby the H_2:CO ratio was varied, and the results were compared to Comparative Catalyst 1 (Pd only). Catalyst 3 performed better in all cases and in particular when H_2 concentration was increased, indicating greater H_2 promotion of the activity for the Pd-Pt alloy, shown in **FIG. 4**. This data suggests that a Pd-Pt alloy is more robust to varying TWC gas conditions.

EXAMPLE 2: VEHICLE TESTING PROCEDURES AND RESULTS

General Synthesis of Catalyst Articles

Catalyst articles with Pd:Pt 100:0, 90:10, 50:50 and 27:73 mol% were prepared following standard washcoat procedure (known to the skilled person), except Pd-DMG (dimethyl glyoxime)basic solution was added to the washcoat in small portions with a solution of HNO_3 to reduce and maintain the pH below 7. The fully formulated catalysts contain 100g/ft^3 Pd or Pd+Pt and 16 g/ft^3 Rh in the following architecture with a Pd top layer:

Top layer: La-doped alumina (0.7 g/ft^3), a rare-earth-doped ceria zirconia (0.7 g/ft^3), Pd(+Pt)-DMG (100 g/ft^3), $BaSO_4$ (200 g/ft^3); and

Bottom layer: La-doped alumina (0.7 g/ft^3), a rare-earth-doped ceria zirconia (0.7 g/ft^3), rhodium (16 g/ft^3).

Table 4: Top Layer PGM loadings of Catalyst Articles in Example 2

	Molar Ratio of Pd: Pt
Comparative Catalyst Article A	100:0
Catalyst Article B	90:10
Catalyst Article C	50:50
Catalyst Article D	27:73

Catalyst Articles in **Table 4** were aged using gasoline engine bench aging, finished under stoichiometric gas mix. The engine bench aging was conducted using a 4.6L engine for 50 hrs using a four mode aging cycle, with a peak bed temperature of about 1000 °C in the catalysts. The catalysts were tested on a 2.4 L vehicle via the FTP drive cycle, emissions measured directly after the catalyst (which is placed in a close-coupled system). The results of the vehicle test are summarized in **FIGs. 5a-c**.

As shown in **FIGs. 5a-5c**, the results show a similar trend to that observed for Catalysts in Example 1. Catalyst Article B showed a ~12% improvement in total accumulated CO emission, marginally better NO_x conversion (<5%) and no deterioration in HC performance, compared Comparative Catalyst Article A.

Within this series of catalyst articles, Pd can be replaced with Pt up to 50 mol% without significantly changing the total emissions and a significant benefit can be observed for Catalyst Article B (with a 90:10 Pd-Pt molar ratio).

EXAMPLE 3: VEHICLE TESTING PROCEDURES AND RESULTS

Comparative Catalyst Article E

First Catalytic Region:

The first catalytic region consists of Pd supported on a washcoat of CeZr mixed oxide, La-stabilized alumina, and Ba promotor, Pd nitrate solution as Pd source was used during the washcoat slurry preparation. The washcoat loading of the first catalytic region was about 1.8 g/in^3 with a Pd loading of 42 g/ft^3.

This washcoat was then coated from the inlet face of a ceramic substrate (600 cpsi, 4.3 mil wall thickness, 118.4 mm in diameter and 91 mm in length) using standard coating procedures with coating depth targeted of 80% of the substrate length, dried at 100 °C.

Second Catalytic Region:

The second catalytic region consists of Rh supported on a washcoat of CeZr mixed oxide, and La-stabilized alumina. The washcoat loading of the second catalytic region was about 1.3 g/in^3 with a Rh loading of 8 g/ft^3.

This second washcoat was then coated from the outlet face of the ceramic substrate containing the first catalytic region from above, using standard coating procedures with coating depth targeted of 80% of the substrate length, dried at 100 °C and calcined at 500 °C for 45mins.

Catalyst Article F

Catalyst Article F according to the present invention was prepared according to the similar procedure as Comparative Catalyst Article E with the exception that partial Pd replacement by Pt in the first catalytic region with Pd loading of 34 g/ft^3 and Pt loading of 8 g/ft^3 and the Pt: Pd molar ratio was about 11:89.

The second catalytic region was the same as Comparative Catalyst Article E.

The fresh Comparative Catalyst Article E and Catalyst Article F were tested over a commercial vehicle equipped with 1.6L turbo engine under Worldwide Light Duty Testing

Procedure (WLTP) with brick placed on closed couple position. vehicle exhaust diluted bag data are shown in **Table 5**.

In addition to the cost saving, surprisingly, Catalyst Article F of the present invention presented excellent activity on NO_x emission control, compared with Comparative Catalyst Article E (*e.g.*, *see* the NO_x performance improved with around 37%).

Table 5: Results of Emissions by Vehicle Diluted Bag Data

	Exhaust Emissions (mg/km)			
	THC	**NMHC**	**CO/10**	**NO_x**
Comparative Catalyst Article E	23	20	28	62
Catalyst Article F	23	19	31	39

EXAMPLE 4: VEHICLE TESTING PROCEDURES AND RESULTS

Comparative Catalyst Article G

First Catalytic Region:

The first catalytic region consists of Pd supported on a washcoat of rare-earth doped CeZr mixed oxide, La-stabilized alumina, and Ba promotor, Pd nitrate solution as Pd source was used during the washcoat slurry preparation. The washcoat loading of the first catalytic region was about 2.0 g/in^3 with a Pd loading of 68 g/ft^3.

This washcoat was then coated on a ceramic substrate (600 cpsi, 3 mil wall thickness, 118.4 mm in diameter and 114.3 mm in length) using standard coating procedures followed by drying at 100 °C.

Second Catalytic Region:

The second catalytic region consists of Rh supported on a washcoat of rare-earth doped CeZr mixed oxide, and La-stabilized alumina. The washcoat loading of the second catalytic region was about 2.0 g/in^3 with a Rh loading of 6 g/ft^3.

This second washcoat was then coated on the ceramic substrate containing the first catalytic region from above, using standard coating procedures, dried at 100 °C and calcined at 500 °C for 45mins.

Catalyst Article H

Catalyst Article H according to the present invention was prepared according to the similar procedure as Comparative Catalyst Article G with the exceptions that partial Pd replacement by Pt in the first catalytic region with Pd loading of 51 g/ft^3 and Pt loading of 17 g/ft^3 (the Pt: Pd molar ratio was about 15:85), and Pd-DMG and Pt-DMG were used instead of Pd nitrate.

The second catalytic region was the same as Comparative Catalyst Article G.

Catalyst Article I

Catalyst Article I according to the present invention was prepared according to the similar procedure as Comparative Catalyst Article G with the exceptions that partial Pd replacement by Pt in the first catalytic region with Pd loading of 34 g/ft^3 and Pt loading of 34 g/ft^3 (the Pt: Pd molar ratio was about 35:65), and Pd-DMG and Pt-DMG were used instead of Pd nitrate.

The second catalytic region was the same as Comparative Catalyst Article G.

Comparative Catalyst Article G and Catalyst Articles H, I were aged using gasoline engine bench aging. The engine bench aging was conducted using a 4.0 L engine for 100 hrs using a lean spike aging cycle, with a peak bed temperature of about 1030 °C in the catalysts. The catalysts were tested on a 2.0 L engine bench via an RDE compatible drive cycle, emissions measured directly after the catalyst (which is placed in a close-coupled system). Summarized vehicle exhaust modal bag data are shown in **Table 6**.

In addition to the cost saving, surprisingly, Catalyst Articles H and I of the present invention presented equivalent activity on THC, CO, and NO_x emission control, compared with Comparative Catalyst Article G.

Table 6: Results of Emissions by Vehicle Modal Data

	Exhaust Emissions (mg/km)		
	THC	**CO/10**	**NO_x**
Comparative Catalyst Article G	107 (+/- 4)	215 (+/-18)	126 (+/- 7)
Catalyst Article H	108 (+/- 4)	199 (+/-15)	126 (+/- 6)
Catalyst Article I	106 (+/- 4)	200 (+/-16)	134 (+/- 9)

The foregoing detailed description has been provided by way of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be apparent to one of ordinary skill in the art and remain within the scope of the appended claims and their equivalents.

Claims

1. A catalyst composition comprising a first platinum group metal (PGM) component and a first support material, wherein the first PGM component comprises platinum (Pt) and palladium (Pd) and is supported on the first support material; and

wherein the first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5.

2. The catalyst composition of claim 1, wherein the Pt:Pd molar ratio is from about 5:95 to about 75:25,

3. The catalyst composition of claim 1 or claim 2, for three-way catalysis.

4. The catalyst composition of any preceding claim, wherein the first PGM component consists of Pt and Pd.

5. The catalyst composition of any preceding claim, wherein the Pt and Pd are at least partially alloyed, preferably substantially alloyed.

6. The catalyst composition of claim 5, wherein the first PGM component consists of an alloy of Pt and Pd.

7. The catalyst composition of any preceding claim, wherein the first support material comprises an inorganic oxide.

8. The catalyst composition of claim 7, wherein the inorganic oxide is selected from one or more of cerium oxide, a ceria-zirconia mixed oxide, an alumina-ceria-zirconia mixed oxide, alumina, magnesia, silica, lanthanum, neodymium, praseodymium, yttrium oxides, and mixed oxides or composite oxides thereof, or a zeolite.

9. The catalyst composition of claim 8, wherein the first support material is selected from alumina, preferably gamma-alumina, a ceria-zirconia mixed oxide, or a combination thereof.

10. The catalyst composition of claim 9, wherein the alumina and/or ceria-zirconia mixed oxide is doped.

11. The catalyst composition of claim 10, wherein the alumina and/or ceria-zirconia mixed oxide is doped with an oxide of one or more of lanthanum, neodymium, yttrium, niobium, praseodymium, hafnium, molybdenum, titanium, vanadium, zinc, cadmium, manganese, iron, copper, calcium, barium, strontium, caesium, magnesium, potassium and sodium, preferably one or more of lanthanum, neodymium, praseodymium and yttrium, more preferably lanthanum.

12. The catalyst composition of claim 10 or claim 11, wherein the dopant is present in the alumina and/or ceria-zirconia mixed oxide in an amount of from 0.001 wt.% to 20 wt.%, preferably from 0.5 wt.% to 10 wt.%.

13. The catalyst composition of any preceding claim further comprising a second PGM component and a second support material.

14. The catalyst composition of claim 13, wherein the second PGM component comprises rhodium (Rh), a Rh alloy, Pt, a Pt alloy, a Rh-Pt alloy or a mixture thereof.

15. A catalyst article for treating exhaust gas comprising:

a substrate; and

a first catalytic region comprising a first platinum group metal (PGM) component and a first support material, wherein the first PGM component comprises platinum (Pt) and palladium (Pd) and is supported on the first support material; and

wherein the first PGM component has a Pt:Pd molar ratio of from about 5:95 to about 95:5.

16. The catalyst article of claim 15, wherein the Pt:Pd molar ratio is from about 5:95 to about 25:75, preferably from about 7:93 to about 20:80, more preferably from about 9:91 to about 15:85, even more preferably from about 9:91 to about 12:88, and most preferably about 10:90.

17. The catalyst article of claim 15 or claim 16, for three-way catalysis.

18. The catalyst article of any of claims 15 to 17, wherein the first PGM component consists of Pt and Pd.

19. The catalyst article of any of claims 15 to 18, wherein the Pt and Pd are at least partially alloyed, preferably substantially alloyed.

20. The catalyst article of claim 19, wherein the first PGM component consists of an alloy of Pt and Pd.

21. The catalyst article of any of claims 15 to 20, wherein the first support material comprises an inorganic oxide.

22. The catalyst article of claim 21, wherein the inorganic oxide is selected from one or more of cerium oxide, a ceria-zirconia mixed oxide, an alumina-ceria-zirconia mixed oxide, alumina, magnesia, silica, lanthanum, neodymium, praseodymium, yttrium oxides, and mixed oxides or composite oxides thereof, or a zeolite.

23. The catalyst article of claim 22, wherein the first support material is selected from alumina, preferably gamma-alumina, a ceria-zirconia mixed oxide, or a combination thereof.

24. The catalyst article of claim 23, wherein the alumina and/or ceria-zirconia mixed oxide is doped.

25. The catalyst article of claim 24, wherein the alumina and/or ceria-zirconia mixed oxide is doped with an oxide of one or more of lanthanum, neodymium, yttrium, niobium, praseodymium, hafnium, molybdenum, titanium, vanadium, zinc, cadmium, manganese, iron, copper, calcium, barium, strontium, caesium, magnesium, potassium and sodium, preferably one or more of lanthanum, neodymium, praseodymium and yttrium, more preferably lanthanum.

26. The catalyst article of claim 24 or claim 25, wherein the dopant is present in the alumina and/or ceria-zirconia mixed oxide in an amount of from 0.001 wt.% to 20 wt.%, preferably from 0.5 wt.% to 10 wt.%.

27. The catalyst article of any of claims 15 to 26 further comprising a second catalytic region.

28. The catalyst article of claim 27, wherein the second catalytic region comprises a second PGM component and a second support material.

29. The catalyst article of claim 28, wherein the second PGM component comprises rhodium (Rh), a Rh alloy, Pt, a Pt alloy, a Rh-Pt alloy or a mixture thereof.

30. The catalyst article of any of claims 27 to 29, wherein the first catalytic region and the second catalytic region form distinct layers and wherein the second catalytic region is deposited directly on the first catalytic region.

31. The catalyst article of any of claims 27 to 29, wherein the first catalytic region and the second catalytic region form distinct layers and wherein the first catalytic region is deposited directly on the second catalytic region.

32. The catalyst article of any of claims 15 to 30, wherein the first catalytic region is supported/deposited directly on the substrate.

33. The catalyst article of any of claims 27 to 29 and 31, wherein the second catalytic region is supported/deposited directly on the substrate.

34. The catalyst article of any of claims 15 to 33, wherein the substrate comprises a first end and a second end with an axial length L.

35. The catalyst article of claim 34, wherein the first catalytic region extends for the entire axial length L.

36. The catalyst article of claim 34 or 35, wherein the second catalytic region extends for the entire axial length L.

37. The catalyst article of claim 34 or 36, wherein the first catalytic region extends for less than the axial length L.

38. The catalyst article of any of claims 34, 35 or 37, wherein the second catalytic region extends for less than the axial length L.

39. The catalyst article of claim 37, wherein the first catalytic region extends from the first end.

40. The catalyst article of claim 37, wherein the first catalytic region extends from the second end.

41. The catalyst article of claim 38, wherein the second catalytic region extends from the first end.

42. The catalyst article of claim 38, wherein the second catalytic region extends from the second end.

43. The catalyst article of any of claims 34 to 42, wherein the first end is an inlet end and the second end is an outlet end of the catalyst article.

44. The catalyst article of any of claims 15 to 43, wherein the first catalytic region comprises from 20 g/ft^3 to 400 g/ft^3 total Pt and Pd, preferably from 30 g/ft^3 to 250 g/ft^3 total Pt and Pd.

45. The catalyst article of any of claims 27 to 44, wherein the second catalytic region comprises from 2 g/ft^3 to 200 g/ft^3 Rh, preferably from 5 g/ft^3 to 100 g/ft^3 Rh.

46. The catalyst article of any of claims 15 to 45, wherein the first catalytic region is the catalyst composition according to any of claims 1 to 12.

47. An emission treatment system comprising the catalyst composition of any of claims 1 to 14 or the catalyst article of any of claims 15 to 46.

48. The emission treatment system of claim 47 for a gasoline engine.

49. The emission treatment system of claim 48, wherein the gasoline engine operates under stoichiometric conditions.

50. A method of treating an exhaust gas, the method comprising:

providing the catalyst composition of any of claims 1 to 14 or the catalyst article of any of claims 15 to 46; and

contacting the catalyst composition or catalyst article with an exhaust gas.

51. The method of claim 50, wherein the exhaust gas is from a gasoline engine.

52. The method of claim 51, wherein the gasoline engine operates under stoichiometric conditions.

53. A method of manufacturing a catalyst article, the method comprising:

providing a slurry comprising:

platinum (Pt) and palladium (Pd) ions in a molar ratio of from about 5:95 to about 95:5, and

a support material;

disposing the slurry on a substrate; and

heating the slurry to form nanoparticles of the Pt and Pd on the support material.

54. The method of claim 53, wherein the slurry comprises one or more of glyoxime; a glyoxime derivative; salicylaldimine, and a salicylaldimine derivative.

55. The catalyst article of any of claims 15 to 46, wherein the catalyst article is obtained or obtainable by the method of claim 53 or 54.

FIG. 1a

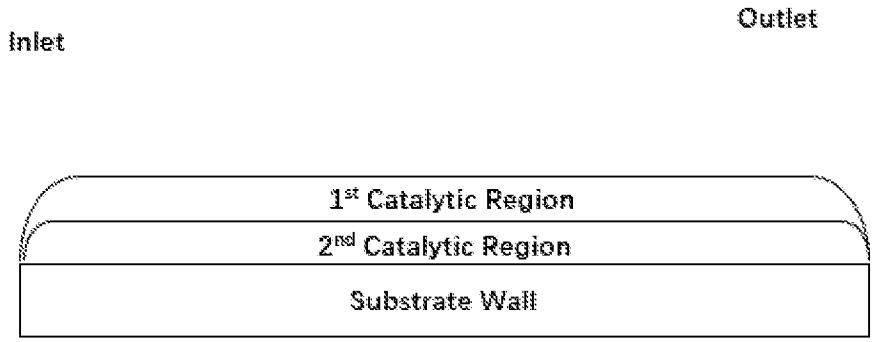

Outlet
Inlet
1st Catalytic Region
2nd Catalytic Region
Substrate Wall

FIG. 1b

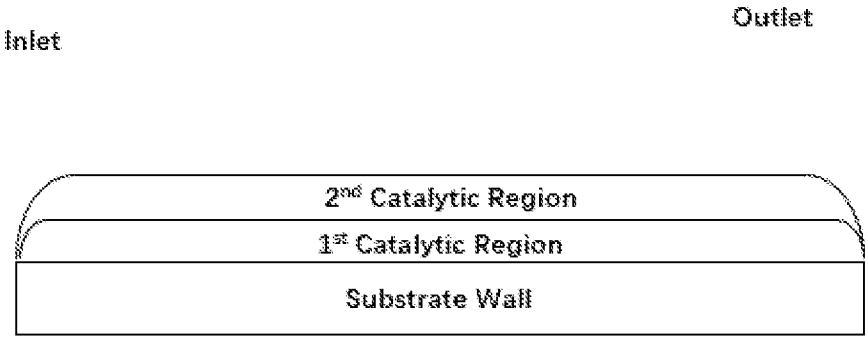

Outlet
Inlet
2nd Catalytic Region
1st Catalytic Region
Substrate Wall

FIG. 2a

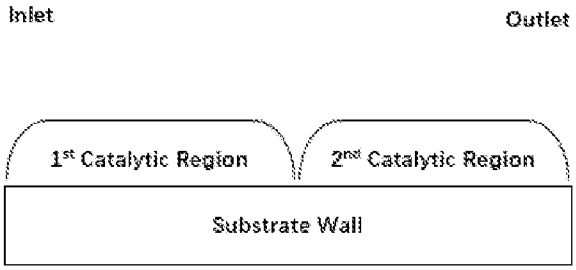


FIG. 2b

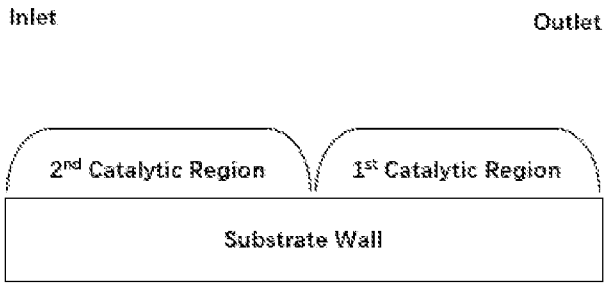


FIG. 2c

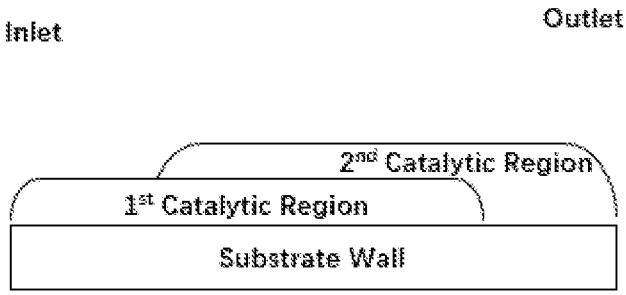


FIG. 2d

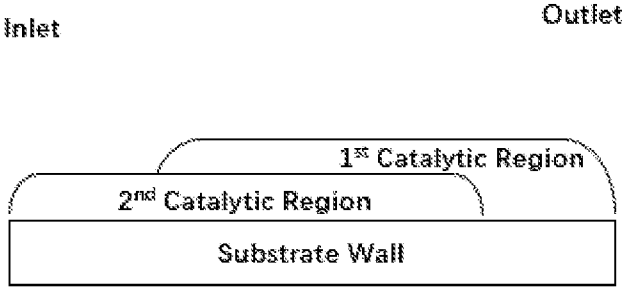


FIG. 3a

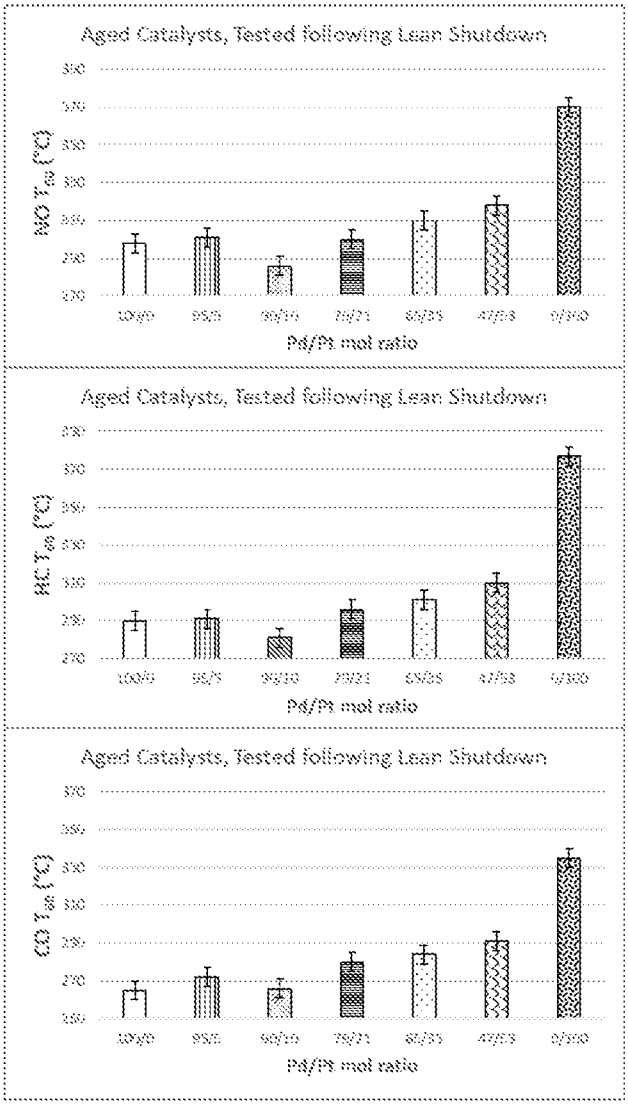

Aged Catalysts, Tested following Lean Shutdown
NO T50 (°C)
Pd/Pt mol ratio
Aged Catalysts, Tested following Lean Shutdown
HC T50 (°C)
Pd/Pt mol ratio
Aged Catalysts, Tested following Lean Shutdown
CO T50 (°C)
Pd/Pt mol ratio

FIG. 3b

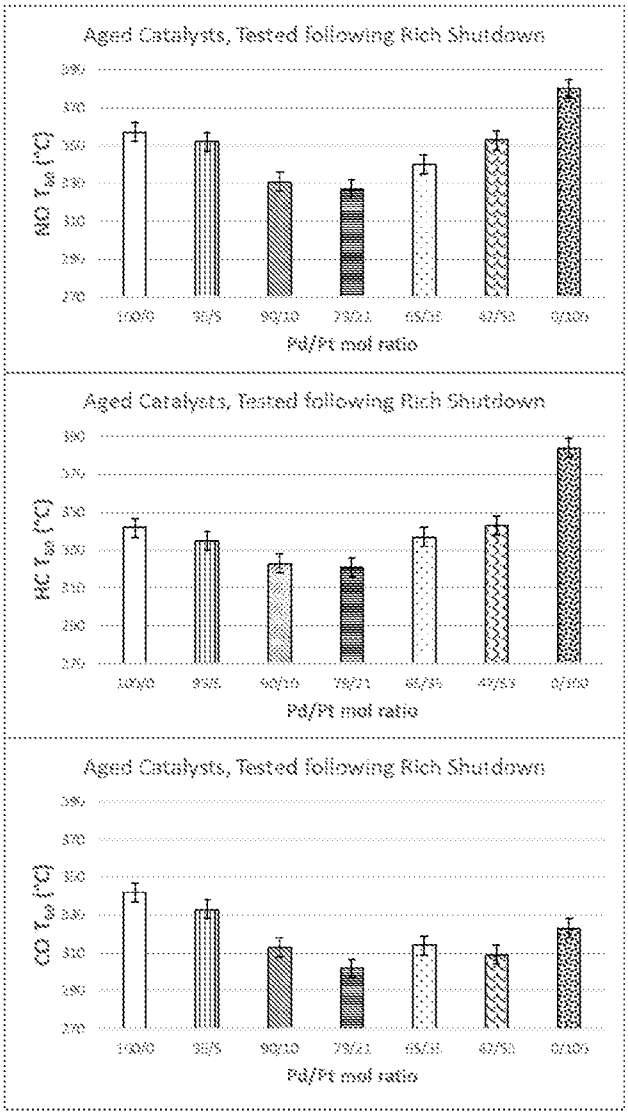

Aged Catalysts, Tested following Rich Shutdown
NO T50 (°C)
Pd/Pt mol ratio
Aged Catalysts, Tested following Rich Shutdown
HC T50 (°C)
Pd/Pt mol ratio
Aged Catalysts, Tested following Rich Shutdown
CO T50 (°C)
Pd/Pt mol ratio

FIG. 4

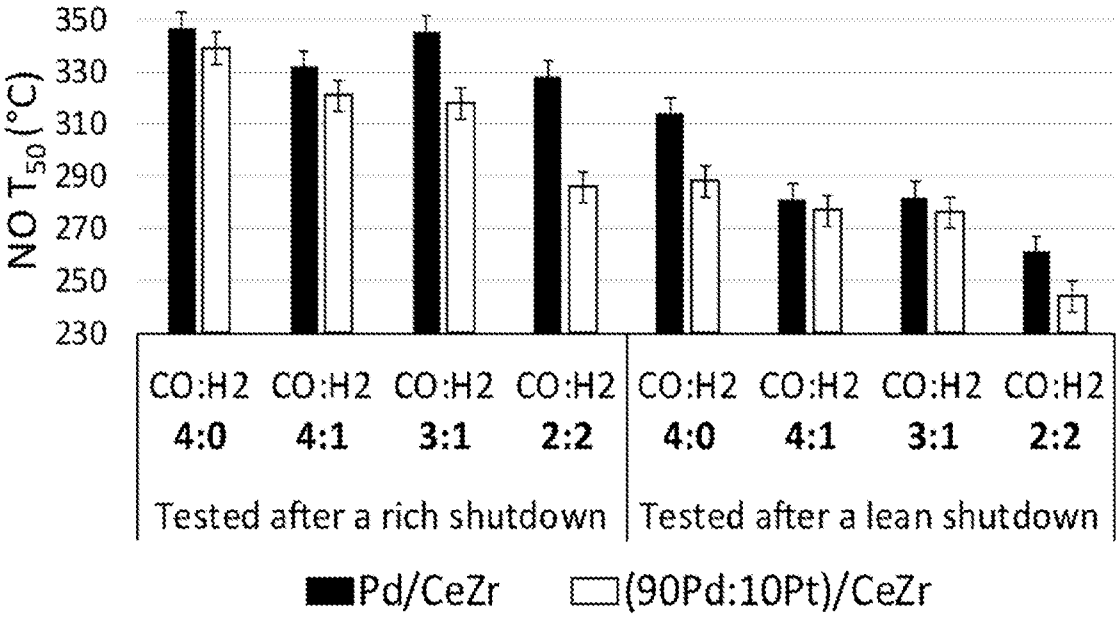

NO T50 (°C)
350
330
310
290
270
250
230
CO:H2 4:0
CO:H2 4:1
CO:H2 3:1
CO:H2 2:2
CO:H2 4:0
CO:H2 4:1
CO:H2 3:1
CO:H2 2:2
Tested after a rich shutdown
Tested after a lean shutdown
Pd/CeZr
(90Pd:10Pt)/CeZr

FIG. 5a

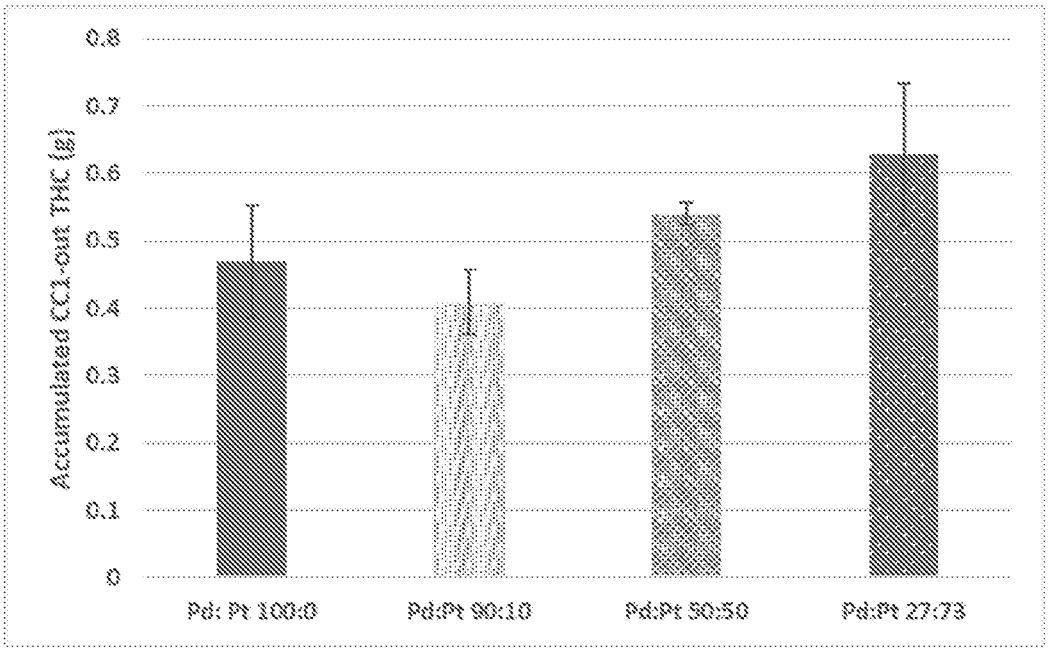

Accumulated CC1-out THC (g)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Pd: Pt 100:0
Pd:Pt 90:10
Pd:Pt 50:50
Pd:Pt 27:73

FIG. 5b

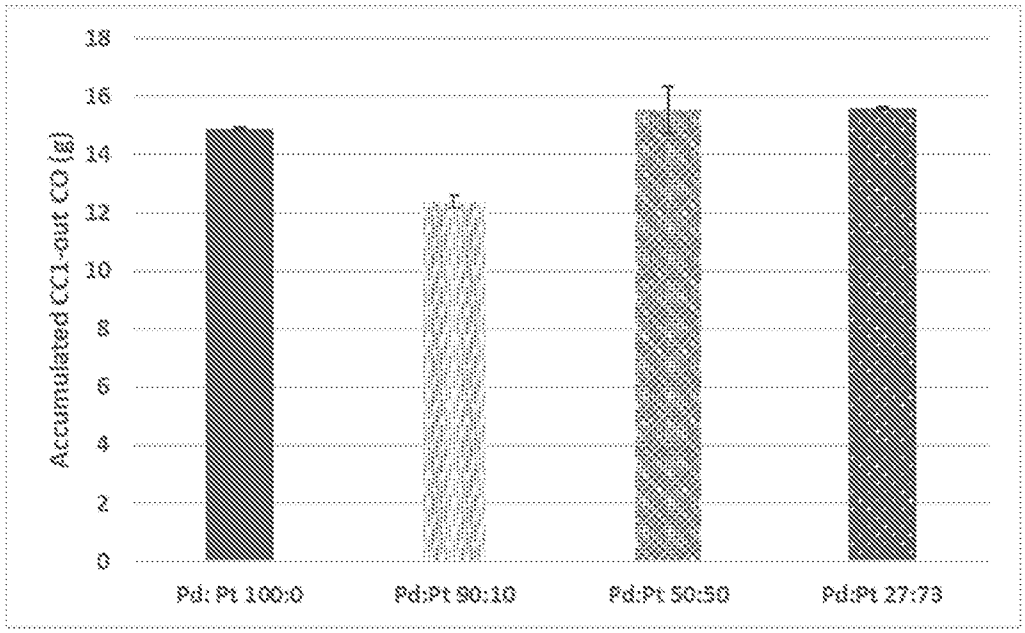
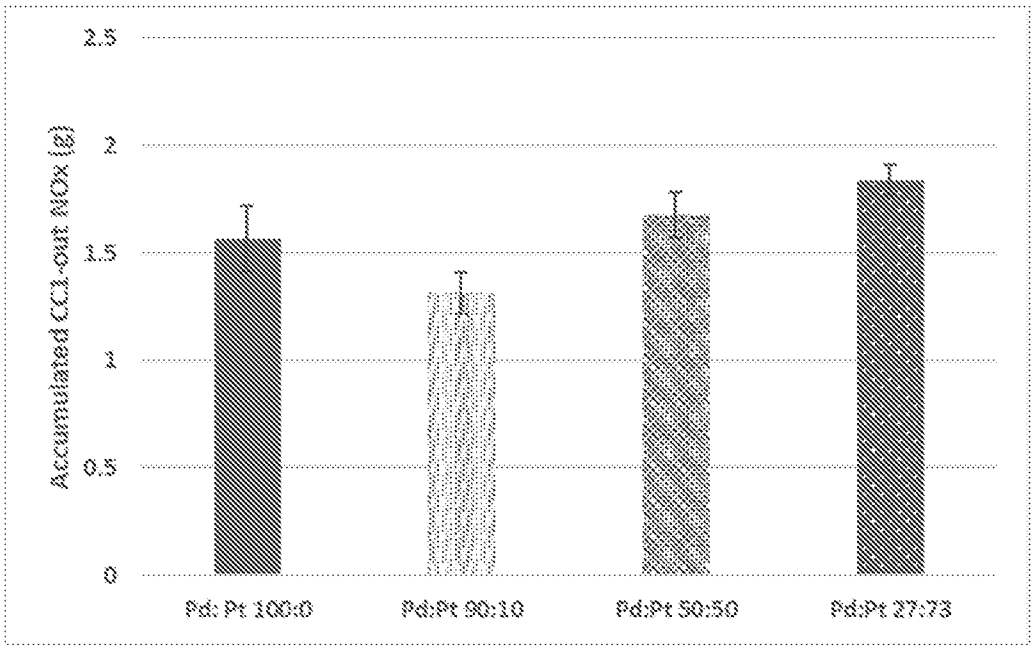

Accumulated CC1-out CO (g)
18
16
14
12
10
8
6
4
2
0
Pd: Pt 100:0
Pd:Pt 90:10
Pd:Pt 50:50
Pd:Pt 27:73

FIG. 5c


Accumulated CC1-out NOx (g)
2.5
2
1.5
1
0.5
0
Pd: Pt 100:0
Pd:Pt 90:10
Pd:Pt 50:50
Pd:Pt 27:73

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2022/052133

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/94 B01J23/56 B01J37/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B01J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2020/024295 A1 (MURESAN NICOLETA [GB] ET AL) 23 January 2020 (2020-01-23) paragraphs [0010], [0082], [0166], [0187] - [0203]; examples 1,2; table 1	1-55
X	US 2011/245073 A1 (OLJACA MIODRAG [US] ET AL) 6 October 2011 (2011-10-06) paragraph [0049]; claims 1,8,14,19,21	1-53,55
X,P	EP 3 991 839 A1 (JOHNSON MATTHEY PLC [GB]) 4 May 2022 (2022-05-04) the whole document	1-55

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 November 2022	05/12/2022

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Gruber, Marco

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2022/052133

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