Method Of Forming Supported Doped Palladium Containing Oxidation Catalysts

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A method of forming a supported oxidation catalyst includes providing a support comprising a metal oxide or a metal salt, and depositing first palladium compound particles and second precious metal group (PMG) metal particles on the support while in a liquid phase including at least one solvent to form mixed metal comprising particles on the support. The PMG metal is not palladium. The mixed metal particles on the support are separated from the liquid phase to provide the supported oxidation catalyst.
FIG. 1A

FIG. 1B
FIG. 2

FIG. 3
Comparison of sonicated pigments in different solvents

**FIG. 4**

**FIG. 5**
METHOD OF FORMING SUPPORTED DOPED PALLADIUM CONTAINING OXIDATION CATALYSTS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of U.S. Non-Provisional patent application Ser. No. 13/758,779 entitled "DOPED PALLADIUM CONTAINING OXIDATION CATALYSTS", filed on Aug. 17, 2012, which is now U.S. Pat. No. 8,562,993, which claims the benefit of Provisional Application Ser. No. 61/524,937 entitled "DOPED PALLADIUM CONTAINING OXIDATION CATALYSTS", filed Aug. 18, 2011, both of which are herein incorporated by reference in their entirety.

U.S. GOVERNMENT RIGHTS

This invention was made with Government support under Florida Hydrogen Initiative Contract #DEFC3604GO14225 awarded by the U.S. Department of Energy. The Government has certain rights in this invention.

FIELD

Disclosed embodiments relate to methods of forming palladium containing catalysts or gas sensors.

BACKGROUND

One of the future alternatives to current fossil-based transportation fuels has been centered on hydrogen gas (H₂). Currently, H₂ is the primary energy source of today's space exploration projects (e.g., as rocket propellant). It is also used in fuel cells that power a variety of machinery including automobiles. Furthermore, H₂ is an important industrial commodity produced and used in many industries. For example, it is used for the reduction of metal oxides (e.g. iron ore), ammonia synthesis, and production of hydrochloric acid, methanol and higher alcohols, aldehydes, hydrogenation of various petroleum, coal, oil shale and edible oils, among others. However, H₂ is a colorless, odorless gas, and is also a flammable gas with a lower explosive limit of about 4% in air. Therefore reliable H₂ sensors are required to detect H₂ leaks wherever H₂ is produced, stored, or used.

To detect H₂, sensors comprising a palladium alloy Schottky diode formed on a silicon substrate are known. These sensors are based on metal-oxide-semiconductor (MOS) technology that is used in the semiconductor industry. The gas sensing MOS structures comprise a H₂-sensitive metal (palladium or its alloy) on a dielectric (e.g., an oxide) adherent to a semiconductor. This H₂ sensor has been commercialized and exploited for detecting H₂ leaks during pre-launches of space vehicles. Others have also used palladium or the like as a sensing element for detecting H₂. A H₂ sensor containing an array of micromachined cantilever beams coated with palladium/nickel has also been disclosed.

Semiconductor materials with a wide band-gap (e.g. gallium nitride) have also been used to make diodes for H₂ detection. One of the concerns for all of these types of sensors using palladium or the like is the requirement of a high operating temperature (greater than 200° C.) and further elevated temperatures (greater than 500° C.) to reactivate the sensing element, bringing about lengthy analysis. Another issue is sensitivity of the sensing element to unintended compounds that are commonly found in the atmosphere, including water vapor, various hydrocarbons, and various reducing gases such as carbon monoxide and hydrogen sulfide. Although not conventionally used, chemochromic H₂ sensors are known. Some chemochromic H₂ sensors lack field stability and have a tendency to crack and peel and some can be washed off by precipitation and/or condensation. Moreover, some chemochromic H₂ sensors do not show selectivity to H₂.

Thus, there remains a need for an improved, reliable and durable chemochromic H₂ sensor, or more generally an oxidation catalyst for a chemochromic reducing gas sensor or catalyst, for a variety of applications, including space, transportation, oil refineries, and chemical plants.

SUMMARY

This Summary is provided to introduce a brief selection of disclosed concepts in a simplified form that are further described below in the Detailed Description including the drawings provided. This Summary is not intended to limit the claimed subject matter's scope.

A method of forming a supported oxidation catalyst includes providing a support comprising a metal oxide or a metal salt, and depositing first palladium compound particles and second precious metal group (PMG) metal particles on the support while in a liquid phase including at least one solvent to form mixed metal comprising particles on the support. The PMG metal is not palladium. The mixed metal particles on the support are separated from the liquid phase to provide the supported oxidation catalyst.

As used herein, a "support" refers to a material in which the palladium compound particles and PMG metal particles are deposited onto in the formation of the supported oxidation catalyst. The support can be in layer form on another layer, such as a layer comprising a plurality of bound particles on a solid surface, or be in discrete particle form.

Disclosed supported oxidation catalysts can be used as a pigment for hydrogen sensing/detection or other sensing/detection of other reducing gases where they may be encapsulated in a reducing gas permeable polymer matrix such as silicone rubber or silicone resin. In another embodiment, the supported oxidation catalyst is used as a catalyst without polymer encapsulation.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a cross sectional depiction of an example supported oxidation catalyst comprising a support, and mixed metal comprising particles on the support including first particles comprising a palladium compound and second particles comprising a precious metal group (PMG) metal, where the PMG is not palladium, according to an example embodiment.

FIG. 1B is a cross sectional depiction of an example encapsulated supported oxidation catalyst comprising the oxidation catalyst in FIG. 1A along with an optional reducing gas permeable polymer that forms a continuous phase which provides complete encapsulation for the support and metal comprising particles, according to an example embodiment.

FIG. 2 shows ΔE vs. exposure time to 100% H₂ gas sensing performance for various disclosed platinum-doped Pd/TiO₂ supported oxidation catalysts used as pigments encapsulated in DOW 734® silicone resin that were synthesized as compared to a known PdO on TiO₂ control (no Pt doping).

FIG. 3 shows ΔE vs. exposure time to 100% H₂ gas sensing performance for various disclosed platinum-doped Pd/TiO₂ supported oxidation catalysts used as pigments encapsulated
in DOW 734® silicone resin that were synthesized having different Pt contents as compared to a known PdO on TiO₂ control (no Pt doping).

FIG. 4 shows Δε vs. exposure time to 100% H₂ sensing gas for various disclosed platinum-doped PdO/TiO₂ supported oxidation catalysts used as pigments encapsulated in DOW 734® silicone resin that were synthesized using different solvents during sonication processing as compared to known PdO on TiO₂ controls (no Pt doping):

FIG. 5 shows Δε vs. exposure time to 100% H₂ sensing gas for various disclosed PdO/BaSO₄ oxidation catalysts (BaSO₄ as supports) used as pigments encapsulated in DOW 734® silicone resin that were synthesized as compared to a known PdO on TiO₂ oxidation catalyst control (no Pt doping).

**DETAILED DESCRIPTION**

Disclosed embodiments in this Disclosure are described with reference to the attached figures, wherein like reference numerals are used throughout the figures to designate similar operations that are not well-known. This Disclosure is not intended to be an exhaustive list of all possible embodiments and includes any and all sub-ranges between (and including) the examples reported as precisely as possible. Any numerical ranges and parameters setting forth the broad scope of this Disclosure are approximations, and the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Moreover, all ranges disclosed herein are to be understood to encompass any and all sub-ranges subsumed therein. For example, a range of “less than 10” can include any and all sub-ranges between (and including) the minimum value of zero and the maximum value of 10, that is, any and all sub-ranges having a minimum value of equal to or greater than zero and a maximum value of equal to or less than 10, e.g., 1 to 5.

Some disclosed embodiments are based on the discovery that a palladium compound oxidation catalyst such as PdO on a support when “doped” with particles comprising a PMG metal provides supported oxidation catalysts which oxidize a reducing gas (e.g., hydrogen, carbon monoxide, or hydrocarbons) with oxidation kinetics sped up significantly and sensitivity increased significantly as compared to the palladium compound (PdO) on the support oxidation catalyst alone. The PMG metal particles feature the metal in its atomic/elemental form which may be clearly contrasted with the form of the metal in metal compounds, such as compounds selected from the group consisting of oxides, hydrides and hydrated oxides of platinum group metals. As well known in metallurgy, physics and chemistry, an elemental (or atomic) metal is in its elemental unchanged state while metals in metal compounds are in an ionic (generally cationic) state. For example, for the conventional PdO pigment, Pd is in the +2 state (Pd²⁺), and as known in the art, and upon exposure to a reducing gas such as H₂, Pd²⁺ reduces to its elemental/atomic form Pd⁰ which results in a visible color change (and the generation of water). An elemental metal such as Pd⁰ cannot itself accept electrons.

Other disclosed embodiments are based on the discovery that the support selection of a material other than titanias such as BaSO₄ also improves oxidation kinetics and detection sensitivity. These embodiments may be combined, by combining doping of the palladium compound (e.g., PdO) with a PMG metal and BaSO₄ supports, which may further improve oxidation kinetics and detection sensitivity.

The support is generally selected so that interaction of the metal particles with the surface of support surfaces minimizing the total energy required for palladium compound (e.g., PdO) reduction. This suggests a small chemical interaction between support and the metal particles and hence destabilization of the palladium compound particles on the surface of the support. For PdO on a TiO₂ support surface, the second PMG metal “dopant” (e.g. Pt) lowers the activation energy required for PdO reduction.

Disclosed supported oxidation catalysts embodied as chemochromic sensors (pigments) change color in a presence of at least one reducing gas. Embodied as chemochromic reducing gas sensors, disclosed reducing gas sensors are irreversible sensors. Disclosed PMG’s can utilize the PMG metals of gold, silver, or platinum group metals, such as ruthenium, rhenium, osmium, iridium, and platinum.

The response time of disclosed chemochromic reducing gas sensors toward H₂ gas by including nanosized PMG dopant particles, wherein the PMG is not palladium, with palladium compound particles (e.g., PdO) has been found to unexpectedly be decreased by about 10 fold while encapsulated in a silicone resin. As noted above, disclosed supported oxidation catalysts can also be used as catalysts, such as to reduce undesirable emissions from fossil fuel powered vehicles.

FIG. 1 is a cross sectional depiction of an example supported oxidation catalyst 100 comprising a support 101 that can comprise a plurality of metal oxide or metal salt (e.g. sulfate or carbonate) particles, first particles 102 comprising palladium compound (e.g., PdO), and second particles 103 comprising a PMG metal wherein the PMG is not palladium, on the support 101, according to an example embodiment. In typical applications, the supported oxidation catalyst 100 can be adhered to a substrate where it can provide its chemochromic reducing gas sensing or catalyst function, such as on a metal wall. The shapes of the support 101, first particles 102 and second particles 103 shown in FIG. 1A are arbitrary.

As noted above, although the support 101 is shown in FIG. 1A in layer form, such as comprising a polycrystalline layer, support 101 may also be in discrete particle form. Typically the support 101 comprises metal oxide or metal salt particles, mixed metal oxide particles, but can also comprise their salts. For pigment (chemochromic) applications, the support 101 comprises particles which are generally colorless, white, or slightly colored. The metal oxide particles can comprise transition metal oxide particles and the metal salt particles can comprise alkaline earth salt particles.

The transition metal oxide particles can comprise Group IV metal oxide particles, such as such ZrO₂, TiO₂, Al₂O₃, or SrZrO₃. The metal salt particles can comprise alkaline earth metal salt particles, such as BaSO₄. The support can also comprise titanium (e.g., embodied as TiO₂), and cerium (e.g.,...
embodied as CeO₂). In one embodiment, the support 101 comprises particles having a size in a range from 0.1 µm to 1.0 µm, and in one particular embodiment from 0.2 µm to 0.25 µm for pigment applications to maximize opacity.

The first particles 102 are palladium compound particles that can comprise palladium oxide, palladium hydride, or a palladium salt. The first particles 102 can have a median size in the range of 2 nm to 8 nm. The second particles 103 are PMG metal particles that can comprise gold, silver, or a PMG metal other than palladium, such as ruthenium, rhodium, osmium, iridium, or platinum. In one embodiment the second particles 103 have a median size in the range from 5 nm to 10 nm. The relative concentration ratio of the second particles 103 to first particles 102 generally range from 1:10 to 1:25 by weight.

The supported oxidation catalyst 100 can further comprise an ultraviolet (UV) absorber or UV Blocker, or a mixture thereof to remedy possible adverse environmental effects. The UV blocker can comprise ZnO₂ or TiO₂. The UV absorber can comprise compounds from the triazine family, such as benzotriazol or benzophenone. The UV absorber or UV Blocker can be in the range of 1-10 wt. % of the supported oxidation catalyst 100. Although not shown in FIG. 1A, UV absorber or UV Blocker particles if shown would be on the support 101 analogous to first particles 102 or second particles 103, or be physically mixed with supported oxidation catalyst 100.

FIG. 1B is a depiction of an example encapsulated supported oxidation catalyst 150 that comprises the supported oxidation catalyst 100 shown in FIG. 1A along with an optional reducing gas permeable polymer 104 that forms a continuous phase (matrix) which provides complete encapsulation for the support 101, first particles 102, and second particles 103, according to an example embodiment. The gas permeable polymer 104 continuous phase can be formed by admixing a suitable material, such as a moisture curable or heat curable silicone sealant with dry catalyst particles or its slurry comprising support particles 101, first particles (palladium compound) 102, and second particles (PMG metal, not palladium) 103 in a liquid phase before drying, and then curing the silicone sealant to form a rubbery gas permeable silicone polymer that forms a continuous phase that provides complete encapsulation.

In some embodiments, the supported oxidation catalyst can comprise a composite layer. A composite layer is known in the material arts and is defined herein as a composite engineered material made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure. In principle, composites can be constructed of any combination of two or more materials, metallic, organic, or inorganic; but the constituent forms are typically more restricted. The matrix provided by the gas permeable polymer 104 is the body constituent, acting as a continuous phase having the other materials referred to as the additive phases embedded therein, with the gas permeable polymer 104 serving to enclose the other composite components and give it bulk form.

Disclosed embodiments also include methods of forming disclosed doped supported oxidation catalysts. A support is provided, such as comprising a plurality of metal oxide or metal salt particles. A palladium compound (e.g., PdO) and a PMG metal other than Pd are deposited on the support(s) in a liquid phase slurry including a solvent to form nanosized palladium compound (e.g., PdO) particles and PMG metal particles other than Pd particles. A solid-liquid separation process such as filtering the slurry allows removal of the liquid phase to form dried solid supported oxidation catalyst which may be referred to as composite particles.

The depositing can comprise co-depositing the palladium compound and PMG metal using a precursor for the palladium compound and a precursor for the PMG metal. As described below, depositing the palladium compound after depositing the PMG metal may provide enhanced sensing performance.

In one embodiment, the method further comprises admixing a moisture curable silicone sealant with the particles in the liquid phase, and then curing the moisture curable silicone sealant to form a rubbery gas permeable silicone polymer. In this embodiment, the gas permeable polymer provides a continuous phase that completely encapsulates the palladium compound particles, the PMG metal particles and the supports.

As noted above, disclosed supported oxidation catalysts can be used in a variety of applications including in the development of chemochromic passive sensors for detecting reducing gases such as hydrogen, carbon monoxide, and hydrocarbons (e.g., natural gas or propane). These gases/liquids are widely used and produced in many industries and a safe operation is a top priority for all of them. Disclosed supported oxidation catalysts can also provide a layer of protection against accidental releases of these gases and therefore reinforces a safe manufacturing/utilization environment. Furthermore, disclosed supported oxidation catalysts can be used as catalysts in the automotive industry to reduce hydrocarbon, carbon monoxide, and NOx emissions, or in any industry that carry methane combustion such as natural gas-powered vehicles. Other example applications include depollution of natural gas-powered vehicles, and catalytic processes for energy production from natural gas.

The effectiveness of gas sensors, such as disclosed supported oxidation catalysts used as chemochromic reducing gas sensors, is typically evaluated by measuring the time necessary to reach a given level of color change, and by determining the total amount of color change. The latter is expressed as ΔE and is measured by a colorimeter. ΔE measures a difference in color by measuring specific parameters of the film (L, a, b). These parameters refer to a color system for measuring absolute chromaticity, L*a*b* color difference Δ(L*a*b*) or ΔE. Color is defined in three dimensions: hue, chroma (saturation) and lightness. L*–the gradient from light to dark, a*–the gradient from red to green, and b*–the gradient from yellow to blue, and ΔE*=(ΔL*)²+(Δa*)²+(Δb*)²)½. This equation gives a standard measurement technique by which one can compare color changes from different chemochromic reducing gas sensor film samples. The greater the ΔE* value, the greater the color contrast. Chemochromic reducing gas sensor films can be analyzed both before and after exposure to the reducing gas, allowing quantification of the intensity of the color change.

EXAMPLES

Disclosed embodiments are further illustrated by the following specific Examples, which should not be construed as limiting the scope or content of this Disclosure in any way.

For example, although Pt metal is generally used as the “dopant” in these examples, Pt can be replaced by gold, silver, or other platinum group metal. Example methods of preparation of disclosed supported oxidation catalysts are now described. Samples referred to as “base” in FIGS. 2-5 such as PK-1-135 NM1 described below refer to known PdO on TiO₂
controls (no Pt metal doping). For testing, the samples were all placed inside a vial and were exposed to 100% H₂ gas with a 45 ml/min flow rate.

Example 1

Depositing 0.3 Wt. % Pt Doping onto PdO/TiO₂ by Reflux

Example 1-A

To deposit PdO particles on TiO₂ (titania), a slurry of 2.5 g TiO₂ in 100 mL water was adjusted to pH 10.6 using 12 M NaOH and stirred at 70°C for an hour. 2.5 mL of 0.281M PdCl₂ solution in 2 M HCl was added dropwise to the mixture, taking care to keep the solution at pH 10.6 using 12 M NaOH. Once all the PdCl₂ solution was added, the pH of the mixture was adjusted to 8 using 3 M HCl. This mixture was stirred and heated for an hour while the PdO was deposited onto the surfaces of the titania. The resulting PdO/TiO₂ solid product was then filtered, washed thoroughly with water, and dried under vacuum at 200°C for 3 hours. The PdO/TiO₂ solid product was used to provide the PK-1-135 NM1 controls.

Example 1-B

0.019 g Na₂PtCl₆ was added to a slurry of 2.5 g PdO/TiO₂ in 100 mL DI water. 0.027 g sodium citrate was added to the mixture, which was then placed under reflux at 70°C and stirred overnight (~16 hours). The Pt on PdO/TiO₂ solid product was filtered, washed thoroughly with water and dried under vacuum at room temperature to provide a disclosed supported oxidation catalysts identified as PK-1-136-NM13.

FIG. 2 which shows ΔE vs. exposure time to 100% H₂ gas for various disclosed Pt doped PdO/TiO₂ supported oxidation catalysts used as pigments encapsulated in DOW 734® silicone resin, along with PK-1-135 NM1 (“Base”) for a PdO on TiO₂ control. The performance of PK-1-136-NM13 can be seen to be similar to PK-1-135 NM1.

PK-1-137-NM15 was prepared by reversing the order of steps 1-A and 1-B. First Pt was deposited onto a TiO₂ support (Step 1-B) and then PdO was deposited onto Pt/TiO₂ by following step 1-A (its ΔE vs. exposure time to 100% H₂ gas is shown in FIG. 2). PK-1-137-NM15 can be seen to provide a significant performance enhancement compared to the PK-1-135 NM1 “base” control and PK-1-136-NM13.

Example 2

Depositing 0.3 Wt.% Pt onto a PdO/TiO₂ Support by Sonication

Example 2A

To deposit PdO, a slurry of 2.5 g TiO₂ in 100 mL water was adjusted to pH 10.6 using 12 M NaOH and stirred at 70°C for an hour. 2.5 mL of 0.281M PdCl₂ solution in 2 M HCl was added dropwise to the mixture, taking care to keep the solution at pH 10.6 using 12 M NaOH. Once all the PdCl₂ solution was added, the pH of the mixture was adjusted to 8 using 3 M HCl. This mixture was stirred and heated for an hour while the PdO was deposited onto the surfaces of the titania. The solid PdO/TiO₂ product was filtered, washed thoroughly with water and dried at room temperature.

Example 2B

Then, 0.019 g Na₂PtCl₆ was added to a slurry of 2.5 g PdO/TiO₂ in 100 mL ethanol to give a loading of 0.3 wt.% Pt on the support. The pH of the solution was adjusted to 6 using 12 M NaOH. Sonication was carried out on the reaction mixture using a direct immersion titanium tip (20 kHz, 100 W cm⁻²) at room temperature. The solid Pt on PdO/TiO₂ product was filtered, thoroughly washed with ethanol, and dried at room temperature and baked at 200°C for 3 hrs to provide PK-1-135-NM-20 (its ΔE vs. exposure time to 100% H₂ gas is shown in FIG. 2). PK-1-135-NM-20 can be seen to provide a significant performance enhancement compared to the PK-1-135 NM1 “base” control.

PK-1-142-NM31 was prepared by reversing the order of steps 2-A and 2-B. First, Pt was deposited onto a TiO₂ support (Step 2-B), and then PdO was deposited onto Pt/TiO₂ by following step 2-A (its ΔE vs. exposure time to 100% H₂ gas is shown in FIG. 2). PK-1-142-NM31 can also be seen to provide a significant performance enhancement compared to the PK-1-135 NM1 “base” control.

Example 3

Synthesis of Irreversible BaSO₄/PdO 3 wt % PdO Chemochromic Pigment (BaSO₄ Supports)

A slurry of 2.5 g BaSO₄ in 100 mL water was adjusted to pH 10.6 using 12 M NaOH and stirred at 70°C for an hour. 2.5 mL of 0.281M PdCl₂ solution in 2 M HCl was added dropwise to the mixture, taking care to keep the solution at pH 10.6 using 12 M NaOH. Once all the PdCl₂ solution was added, the pH of the mixture was adjusted to 7 using 3 M HCl. This mixture was stirred and heated for an hour while the PdO was deposited onto the surfaces of the BaSO₄. The solid product was filtered, washed thoroughly with water and dried under vacuum at 110°C for 3 hours to provide PK-2-124-NM48C1 (shown in FIG. 5). The catalyst PK-2-124-NM55 (shown in FIG. 5) was synthesized by adding ethanol to PK-1-124-NM48C1 and sonicing the slurry using a direct immersion titanium tip (20 kHz, 100 W cm⁻²) at room temperature. PK-2-124-NM55 can be seen in FIG. 5 to provide a significant performance enhancement compared to the PK-2-50 NM1-1 “base” control.

Example 4

Exposure of Pt-Doped PdO/TiO₂ Pigments to 100% Hydrogen Gas

A series of disclosed platinum-doped PdO/TiO₂ (PdO—Pt/TiO₂) pigments were synthesized. Four pigments were synthesized by adding 0.3 Wt. % of Pt to PdO on TiO₂ in different orders and different synthesize procedures. FIG. 2 shows ΔE vs. exposure time performance for various disclosed platinum-doped PdO/TiO₂ pigments encapsulated in DOW 734® silicone resin that were synthesized.

All pigments with Pt dopants were found to have an overall higher sensitivity to 100% H₂ gas as compared to the PK-1-135 NM1 PdO on TiO₂ controls (no Pt doping), except for when the Pt was first deposited on TiO₂ support under reflux condition (PK-1-136-NM13). However, when Pt was deposited on PdO/TiO₂ particles using sonication technique, a 10 fold improvement of pigment response time toward H₂ gas (start of visible color change, i.e. ΔE=10) was observed (sample PK-1-135-NM20). This encapsulated pigment showed a visible color change within first 10 seconds after exposure to H₂ gas.

Furthermore, FIG. 3 shows ΔE vs. exposure time to 100% H₂ gas sensing performance for various disclosed platinum-doped PdO/TiO₂ supported oxidation catalysts used as pig-
ments encapsulated in DOW 734® silicone resin that were synthesized having different Pt contents as compared to a known PdO on TiO2 control (no Pt doping). As shown in FIG. 3, the amount of Pt can be reduced to as low as 0.075 wt. % without any significance loss in response time toward hydrogen gas compared to composite particles with 0.3 wt % of Pt dopant (see FIG. 3).

Example 5

Effect of Solvent on Platinum-Doped PdO/TiO2 Pigments

FIG. 4 shows AE vs. exposure time performance for a synthesized platinum-doped PdO/TiO2 pigments encapsulated in DOW 734 silicon resin synthesized using water, instead of ethanol as the solvent during sonication procedure. This example showed that platinum-doped pigments synthesized in ethanol are far superior in response time toward H2 compared to pigments synthesized in water (PK-1-138-NM16). When Pt was deposited using water as sonic solvent, the pigment showed no measurable improvement over non-doped PdO/TiO2 pigments reflected in the PK-1-135 NM1 base/control (PdO on TiO2) controls (no Pt doping):

Example 6

Exposure of PdO/BaSO4 Pigments (BaSO4 Supports)

FIG. 5 shows AE vs. exposure time performance for two synthesized PdO/BaSO4 pigments (see PK-2-124-NM48C-1 and PK-2-142-NM55 in FIG. 5) encapsulated in DOW 734 silicon resin. The PdO/BaSO4 oxidation catalysts were prepared by sonication showed a response time very similar to Pt doped PdO/TiO2 catalyst shown as PK-2-125-NM-20-2. This BaSO4-based catalyst has eliminated the need for PMG metal dopant, and therefore will be more cost effective. However, BaSO4 can be used with PMG metal dopants for even faster kinetics.

While various disclosed embodiments have been described above, it should be understood that they have been presented by way of example only, and not limitation. Numerous changes to the subject matter disclosed herein can be made in accordance with this Disclosure without departing from the spirit or scope of this Disclosure. In addition, while a particular feature may have been disclosed with respect to only one of several implementations, such feature may be combined with one or more other features of the other implementations as may be desired and advantageous for any given or particular application.

Thus, the breadth and scope of the subject matter provided herein should not be limited by any of the above explicitly described embodiments. Rather, the scope of this Disclosure should be defined in accordance with the following claims and their equivalents.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. Furthermore, to the extent that the terms “including,” “includes,” “having,” “has,” “with,” or variants thereof are used in either the detailed description and/or the claims, such terms are intended to be inclusive in a manner similar to the term “comprising.”

Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

The invention claimed is:

1. A method of forming a supported oxidation catalyst, comprising:
   providing a support comprising a metal oxide or a metal salt,
   and depositing first palladium compound particles and second precious metal group (PMG) metal particles on said support while in a liquid phase including at least one solvent to form mixed metal comprising particles on said support, wherein said second PMG metal particles is not palladium, and separating said mixed metal comprising particles on said support from said liquid phase to provide said supported oxidation catalyst.

2. The method of claim 1, wherein said first palladium compound particles comprise palladium oxide, palladium hydroxide, or a palladium salt.

3. The method of claim 1, wherein said second PMG metal particles are nanosized and a relative concentration ratio of said second PMG metal particles to said first palladium compound particles ranges from 1:10 to 1:25 by weight.

4. The method of claim 1, wherein said second PMG metal particles comprise gold, silver or platinum.

5. The method of claim 1, wherein said separating comprises drying and said depositing comprises co-depositing said first palladium compound particles and said second PMG metal particles using a precursor for said first palladium compound particles and a precursor for said second PMG metal particles.

6. The method of claim 5, wherein said co-depositing comprises depositing said first palladium compound particles after depositing said second PMG metal particles.

7. The method of claim 1, further comprising:
   admixing a moisture or heat curable silicone sealant with said first palladium compound particles and said second PMG metal particles, and curing said silicone sealant to form a rubbery gas permeable silicone polymer, wherein said gas permeable silicone polymer provides a continuous phase that completely encapsulates said supported oxidation catalyst.

8. The method of claim 1, wherein said solvent comprises an alcohol and said depositing comprises sonication.

9. The method of claim 8, wherein said alcohol comprises ethanol.

10. The method of claim 1, wherein said support comprises BaSO4.

11. A method of forming a supported oxidation catalyst, comprising:
   providing a support comprising a metal oxide or a metal salt,
   depositing first palladium compound particles and second platinum metal particles on said support while in a liquid phase including at least one solvent to form mixed metal comprising particles on said support, and separating said mixed metal comprising particles on said support from said liquid phase to provide said supported oxidation catalyst.

12. The method of claim 11, further comprising:
   admixing a moisture or heat curable silicone sealant with said first palladium compound particles and said second platinum metal particles on said support while in a liquid phase including at least one solvent to form mixed metal comprising particles on said support, and separating said mixed metal comprising particles on said support from said liquid phase to provide said supported oxidation catalyst.
platinum metal particles, and curing said silicone sealant to form a rubbery gas permeable silicone polymer, wherein said gas permeable silicone polymer provides a continuous phase that completely encapsulates said supported oxidation catalyst.