

EXHAUST GAS EMISSIONS ABATEMENT SYSTEM

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application benefits from the priority of U.S. Provisional Patent Application No. 63/044,002, entitled "EXHAUST GAS EMISSIONS ABATEMENT SYSTEM," filed June 25, 2020, which is hereby incorporated by reference in its entirety.

5 BACKGROUND OF THE DISCLOSURE

[0002] The present disclosure relates generally to the field of abating exhaust gas emissions and specifically to abating methane emissions from natural gas fueled engines. More specifically, the present disclosure relates to a dual bed methane emissions abatement system having a guard bed for converting, capturing, or otherwise removing methane
10 oxidation catalyst poisons from exhaust gas generated from natural gas fuel engines and a methane oxidation catalyst (MOC) bed for converting and abating the methane emissions in the exhaust gas.

[0003] Natural gas is an abundant and economical alternative to oil-derived fuels such as gasoline, kerosene and diesel. Accordingly, manufactures of engines used in stationery
15 and transport applications/service are shifting their attention and efforts from oil-derived fuels to compressed natural gas (CNG) or liquefied natural gas (LNG) as fuels. Both CNG and LNG are less expensive and burn cleaner than oil-derived fuels. For example, compared to certain oil-derived fuels, CNG and LNG, when burned, emit approximately 75% less greenhouse gases such as carbon dioxide (CO₂), carbon monoxide (CO) and
20 nitrogen oxides (NO_x). In addition, the CNG and LNG produce significantly less particulates relative to oil-derived fuels. CNG and LNG are primarily (> 90%) composed

of methane (CH_4). CH_4 is a more potent greenhouse gas than CO_2 . Therefore, while using CNG and LNG decreases overall emissions compared to oil-derived fuels, incomplete burning of CNG and LNG may result in undesirable emissions of CH_4 , i.e. high CO_2 equivalent. Therefore, there is a current need to treat engine exhaust gases generated from
5 burning of CNG or LNG fuels in order to remove or abate the undesirable CH_4 emissions before releasing the exhaust gas from the system.

SUMMARY

[0004] In a first embodiment, a system for removing methane oxidation catalyst (MOC) poisons from an exhaust gas including a methane abatement unit that may receive the
10 exhaust gas having methane (CH_4) and the MOC poisons. The methane abatement unit includes a guard bed that may remove the MOC poisons from the exhaust gas and may generate an intermediate exhaust gas having the CH_4 and devoid of the MOC poisons. The guard bed includes a MOC poisons capturing component having a first transition metal oxide, an aluminum oxide (Al_2O_3) support material, and a dolomite-derived support
15 material. The methane abatement unit also includes a MOC bed fluidly coupled to and positioned downstream from the guard bed. The MOC bed includes a MOC and may remove CH_4 from the intermediate exhaust gas to generate a treated exhaust gas having less than approximately 200 parts per million volume (ppmv) CH_4 .

[0005] In another embodiment, a method for removing methane oxidation catalyst (MOC) poisons from an exhaust gas including feeding the exhaust gas having methane (CH_4) and
20 the MOC poisons to a methane abatement unit including a guard bed and a MOC bed fluidly coupled to and downstream from the guard bed and contacting the exhaust gas with

a MOC poisons capturing component disposed within the guard bed. The MOC poisons capturing component includes a first transition metal oxide, an aluminum oxide (Al_2O_3) support material, and a dolomite-derived support material. The method also includes removing the MOC poisons from the exhaust gas to generate an intermediate exhaust gas
5 devoid of MOC poisons and comprising the CH_4 .

[0006] In another embodiment, a methane oxidation catalyst (MOC) poisons capturing component for removing MOC poisons from an exhaust gas including an aluminum oxide (Al_2O_3) support material having a first porosity, a dolomite-derived support material having a second porosity that is less than the first porosity, and a first transition metal
10 oxide supported on the Al_2O_3 support material, the dolomite-derived support material, or both. A concentration of the first transition metal oxide is between approximately 1-25 weight % (wt %) and the MOC poisons capturing component removes sulfur dioxide (SO_2), phosphorus (P), calcium (Ca), zinc (Zn), silicon (Si) and ash.

[0007] Additional features and advantages of exemplary implementations of the disclosure
15 will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by the practice of such exemplary implementations. The features and advantages of such implementations may be realized and obtained by means of the instruments and combinations particularly pointed out in the appended claims. These and other features will become more fully apparent from the following description, and
20 appended claims, or may be learned by the practice of such exemplary implementations as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Advantages of the disclosure may become apparent upon reading the following detailed description and upon reference to the drawings in which:

[0009] FIG. 1 is a block diagram of a system including a natural gas fueled engine that
5 generates an exhaust gas and an exhaust emissions abatement system having a dual bed methane abatement unit having a methane oxidation catalyst (MOC) poisons capturing component, in accordance with an embodiment of the present disclosure;

[0010] FIG. 2 is a block diagram of the dual bed methane abatement unit that may be used with the system of FIG. 1, the dual bed methane abatement unit includes a guard bed having
10 the MOC poisons capturing component positioned upstream of a MOC bed, in accordance with an embodiment of the present disclosure;

[0011] FIG. 3 is a block diagram of a multi-layer guard bed that may be used in the dual bed methane abatement unit of FIG. 2, whereby the multi-layer guard bed includes a first layer having a first MOC poisons capturing component and a second layer having a second
15 MOC poisons capturing component, in accordance with an embodiment of the present disclosure;

[0012] FIG. 4 is a block diagram of a single layer guard bed that includes at least one MOC poisons capturing component and may be used in the dual bed methane abatement unit of FIG. 2, in accordance with an embodiment of the present disclosure;

[0013] FIG. 5 is an exemplary plot of percent CH₄ conversion as a function of time on stream (TOS) for the guard bed (GB) and MOC system of FIG. 1, in accordance with an embodiment of the present disclosure;

5 [0014] FIG. 6 is an exemplary plot of MOC catalyst poisons concentration distribution profiles as a function of guard bed length, in accordance with an embodiment of the present disclosure;

[0015] FIG. 7 is an exemplary plot of MOC catalyst poisons concentrations distribution profiles as a function of MOC monolith length, in accordance with an embodiment of the present disclosure;

10 [0016] FIG. 8 is an exemplary plot of percent methane conversion as a function of time on stream obtained at a temperature of 425 °C for various guard bed formulations positioned upstream of the MOC, in accordance with an embodiment of the present disclosure;

[0017] FIG. 9 is an exemplary plot of percent methane conversion as a function of time on stream obtained at a temperature of 470 °C for various guard bed formulations positioned
15 upstream of the MOC, in accordance with an embodiment of the present disclosure; and

[0018] FIG. 10 is a flow diagram of a method for treating an exhaust gas produced by a natural gas fueled engine, having methane and MOC poisons using the system of FIG. 1, in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

- [0019] One or more specific embodiments of the present disclosure will be described below. These described embodiments are examples of the presently disclosed techniques, which include system, guard bed, and method of use of the system to treat an exhaust gas generated by the system to abate the methane emissions from natural gas fueled engines). Additionally, in an effort to provide a concise description of these embodiments, not all features of an actual implementation may be described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions will be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure.
- [0020] When introducing elements of various embodiments of the present disclosure, the articles "a," "an," and "the" are intended to mean that there are one or more of the elements. The terms "comprising," "including," and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements. Additionally, it should be understood that references to "one embodiment" or "an embodiment" of the present disclosure are not intended to be interpreted as excluding the existence of additional embodiments that also incorporate the recited features.

[0021] The terms “approximately,” “about,” and “substantially” as used herein represent an amount close to the stated amount that still performs a desired function or achieves a desired result. For example, the terms “approximately,” “about,” and “substantially” may refer to an amount that is within less than 10% of, within less than 5% of, within less than 1% of, within less than 0.1% of, and within less than 0.01% of a stated value.

[0022] Natural gas contains between approximately 70% to approximately 95% of methane (CH_4). Natural gas, in the form of compressed natural gas (CNG) and/or liquified natural gas (LNG), is more and more utilized as a fuel in place of or in parallel with oil-derived fuels (e.g., gasoline, coal, etc.) for engines in stationary (power, drilling etc.) and transport (marine, railroad, and other on road) applications. For example, an internal combustion engine may combust natural gas (e.g., CNG and LNG) to produce a combustion gas that contains energy that is extracted by the engine components (e.g., pistons, turbines, etc.) to provide power to the system. The combustion gas may contain unburned methane, oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), water (H_2O), nitrogen (N_2) and other gases that exit the system as exhaust gas. The combustion gas from the natural gas engine also contains small levels of sulfur dioxide (SO_2). The SO_2 in the combustion gas results from small levels (between approximately 0.1 to approximately 8 parts per million (ppm)) of sulfur (S) present in the natural gas as well as that present in the diesel pilot (e.g., for dual fuel engines) and in the lubrication oil. For example, for spark ignited natural gas engines, the level of SO_2 in the combustion gas is dependent on the level of S in the natural gas fuel and the S level in the oil as well as on the fuel and oil consumption rates. In addition to the SO_2 , the combustion

gas from natural gas engines also contains small (approximately less than 3000 ppm) levels of other chemical species such as ones having phosphorus (P), zinc (Zn), calcium (Ca), silicon (Si) and others. These latter species are typically present in oil additives. Accordingly, their presence and concentration in the combustion gas is attributable to the consumption of oil and oil consumption rate, respectively. The amount of residual non-methane hydrocarbons (NMHC), particulate matter (ash), CO₂ and other emissions present in the exhaust gas generated from combustion of natural gas is significantly less than the amounts of NMHC, PM and CO₂ present in an exhaust gas generated from combustion of oil-derived fuels. Accordingly, the use of natural gas for power generation decreases these particular emissions compared to oil-derived fuels.

[0023] However, under certain operating conditions, natural gas fueled engines may not completely burn CH₄. Accordingly, the unburned CH₄ may slip into the exhaust gas and be released from the system. For example, natural gas engines operating under lean fuel (e.g., an oxygen-rich fuel) regime, may generate exhaust gas having between approximately 200 parts per million volume (ppmv) to approximately 3000 ppmv CH₄. It has been recognized that CH₄ is a more potent greenhouse gas compared to CO₂ (e.g., 1 mol of CH₄ ≥ 25 CO₂ mol equivalents). Therefore, it is desirable to develop and deploy an exhaust gas emissions abatement system that may remove or decrease the amount of CH₄ slip in such a way so that the CH₄ level in the exhaust gas is at or below regulated emission levels (e.g., below approximately 150 to 200 ppmv).

[0024] One technique for CH₄ abatement includes oxidation of methane in the presence of a methane oxidation catalyst (MOC). In methane oxidation techniques, hot CH₄-containing exhaust gas contacts the MOC, which in the presence of O₂ catalytically

converts CH₄ into CO₂ and H₂O. MOCs generally used for CH₄ abatement include at least one active metal oxide supported on a porous inorganic oxide support. By way of non-limiting example, MOCs that may be used for CH₄ oxidation or abatement may include noble metal oxides, such as platinum (Pt), palladium (Pd), silver (Ag), iridium (Ir),
5 ruthenium (Ru), rhodium (Rh), osmium (Os) and gold (Au), base metals (e.g., barium (Ba), cesium (Cs), etc.), and rare earth elements (cerium (Ce), yttrium (Y), lanthanum (La), Neodymium (Nd), etc.). In certain embodiments, the MOC may include other elements as dopants or promoters. In addition, the MOC's may contain various porous inorganic oxides as supports (e.g., aluminum oxide (Al₂O₃), titanium oxide (TiO₂), zirconium oxide (ZrO₂),
10 etc.) and mixtures thereof. As appreciated by a person of ordinary skilled in the art, Pd-(in the form of PdO) based MOC's exhibits the highest activity in methane oxidation, i.e. ability to convert and abate methane emissions favorably at the reaction temperatures >300 °C. However, noble metal oxide catalysts and in particular PdO-based MOC, are very sensitive to chemical species such as SO₂, P, Zn, Ca, and Si that are generally present in
15 the exhaust gas. As such, the performance of the MOC for methane oxidation is adversely affected by some of these chemical species. Hereinafter the chemical species SO₂, P, Zn, Ca, and Si, among others, are referred to as MOC poisons. These poisons adversely affect the activity of the MOC for methane oxidation, i.e. the MOC's ability to convert/abate CH₄ as well as its performance stability and useful life. The catalyst poisons exert their adverse
20 effect on the MOC by chemically reacting with or physically covering or adsorbing on the active centers of the MOC, and thus preventing the MOC from fully exerting its methane oxidation activity. The main active sites on PdO-based MOCs are oxygen vacancies on the PdO. The methane oxidation reaction proceeds via an intermediate complex formed

between these oxygen vacancies and the CH₄ molecules in the exhaust gas. The
aforementioned catalyst poisons chemically react with the oxygen vacancies on the Pd or
physically cover the active sites. As such, the catalyst poisons effectively prevent the
active sites from being accessed by and reacting with methane, and thus rendering them
5 inactive for methane oxidation.

[0025] For example, at optimal methane oxidation exhaust gas temperatures (e.g.,
between approximately 300 °C and 600 °C and more specifically between 400 °C and 530
°C), oxygen vacancies in the PdO react with SO₂, or its oxidized form SO₃, present in the
exhaust gas to form stable palladium sulfate (PdSO₄). Palladium sulfate is inactive for CH₄
10 oxidation. Additionally, PdSO₄ cannot be decomposed under typical CH₄ oxidation
conditions and in the optimal methane oxidation exhaust gas temperatures. Therefore, the
catalytic activity and the overall catalyst performance stability/life of the PdO-based MOC
in the presence of SO₂ in exhaust gas is adversely affected by the formation of PdSO₄.
Other catalyst poisons such as P, Zn, Ca, Si, and ash may also react with or physically
15 cover the active sites in the MOC, and thus further contribute to the overall decrease in
methane oxidation activity and deactivation of the MOC. Therefore, it may be desirable
to develop and deploy, in conjunction with natural gas engines, sulfur and other catalyst
poisons capturing devices and techniques in order to remove the catalyst poisons and allow
for maintaining the catalytic performance of MOCs placed downstream of such devices at
20 its peak level.

[0026] The present disclosure provides embodiments of an exhaust gas emissions
abatement system and a method of use, whereby the exhaust gas emission abatement
system that includes a dual bed methane abatement unit having a guard bed and a MOC

that effectively remove MOC catalyst poisons and abate CH₄ emissions from natural gas fueled engines. In addition, the present disclosure provides embodiments of improved guard bed formulations for removal of the MOC catalyst poisons. As discussed in further detail below, the guard bed is positioned upstream of a MOC bed and may include one or
5 more layers of one or more components that convert, capture, or remove, to large extent, the MOC catalyst poisons from the exhaust gas. In this way, the catalyst poisons in the exhaust gas are removed prior to feeding the exhaust gas to the MOC. This allows for the MOC catalyst to fully exert its peak activity and performance in methane oxidation/abatement and therefore, could pave the way for a commercially viable exhaust
10 gas emissions abatement system to abate methane emissions from natural gas engines in stationary or transport service.

[0027] With the foregoing in mind, **FIG. 1** is a block diagram of an embodiment of a power generation system **10** that may include an exhaust gas emissions abatement system, in accordance with the present disclosure. In operation, the system **10** receives and
15 consumes natural gas to generate power and exhaust gas as a byproduct. As discussed in further detail below, the exhaust gas emissions abatement system treats the exhaust gas in a methane abatement unit to produce treated exhaust gas. In the illustrated embodiment, the system **10** includes a natural gas engine **12** and an exhaust gas emissions abatement system **14** downstream of the natural gas engine **12**. The natural gas engine **12** may be a
20 spark ignited engine or dual fuel engine. For example, the natural gas engine **12** may be a heavy-duty engine used in stationary application (e.g., compressor, drilling, and power generation) or one used in transport application (e.g., on road, mining, marine, and rail).

[0028] During operation, the natural gas engine **12** receives a natural gas fuel **18** and air **20** and combusts the air-fuel mixture to generate power **24** and an exhaust gas **28**. In a spark ignited natural gas engine, the air-fuel mixture is compressed in the cylinders and then sparked with the aid of a spark plugs to provide for the combustion of the mixture. In
5 a dual fuel engine, the natural gas engine **12** may receive a second fuel (e.g., diesel) in addition to the natural gas fuel **18**. The amount of the second fuel (diesel) is significantly less (generally between approximately 5-10 % of the total fuel) relative to the amount of the natural gas fuel. In this particular instance, the second fuel (diesel) is used as a pilot to spark the main natural gas fuel.

10 [0029] The natural gas engine **12** may operate in either fuel-lean burn mode or fuel-rich burn mode. In the fuel-lean burn mode, the natural gas engine **12** burns the fuel **18** with an excess amount of the air **20** (e.g., oxygen). For example, the air **20** and the fuel **18** may be provided to the natural gas engine **12** in a different ratio. Depending on whether the amount of oxygen in the air (and the total amount of air) is sufficient, larger, or smaller
15 than required to completely burn the fuel, the type of engine operation regime is defined as stoichiometric, fuel-lean (or lean), or fuel rich (or rich). Normally, the burn? type is defined by the air to fuel (AFR) ratio. The AFR ratio may be expressed as the mass of air vs the mass of fuel present in the engine. The AFR value for stoichiometric burn of natural gas is approximately 17.2:1. This implies that in order to have a stoichiometric burn 17.2 parts
20 of air and 1 part of fuel are required. Therefore, an $AFR < 17.2$ corresponds to fuel-rich burn, whereas an $AFR > 17.2$ corresponds to a fuel-lean burn.

[0030] By operating the natural gas engine **12** in a fuel-lean burn mode, at least a portion of the oxygen (O_2) in the air **20** of the air-fuel mixture remains unreacted and exits

the natural gas engine **12** along with the exhaust gas **28**. The unreacted O₂ in the exhaust gas **28** may be used by the MOC to oxidize the unburned CH₄ present in the exhaust gas **28**.

[0031] In accordance with the present disclosure, the fuel **18** is natural gas in the form of compressed natural gas (CNG), liquified natural gas (LNG), or both. In certain embodiments, the fuel **18** may be a mixture of natural gas and one or more hydrocarbon fuels such as, but not limited to, gasoline, kerosene, diesel, or gasoil. As used herein, “natural gas” is intended to denote a mixture of hydrocarbons having carbon numbers ranging from 1 to 6 (C₁-C₆ hydrocarbons) containing more C₁ hydrocarbons (e.g., methane (CH₄)) than the total amount of C₂-C₆ hydrocarbons. Hydrocarbons having a carbon number from 1 to 6 include, but are not limited to, CH₄, ethane (C₂H₆), propane (C₃H₈), butanes (C₄H₁₀), pentanes (C₅H₁₂), and hexanes (C₆H₁₄). In accordance with the present embodiments, the natural gas may have between approximately 50 percent (%) and approximately 95% or more by volume of CH₄. For example, the natural gas may have at least 70% by volume, at least 90% by volume, or at least 95% by volume CH₄.

[0032] Following combustion, the natural gas engine **12** directs the exhaust gas **28** to the exhaust gas emissions abatement system **14**. The exhaust gas emissions abatement system **14** includes a methane abatement unit **30**, which treats the exhaust gas **28** to convert, capture, and, to a large extent remove undesirable chemical species such as various catalyst poisons (SO₂, P, Zn, Ca, Si, etc.) and CH₄, NO_x, and other combustion by-products from the exhaust gas **28** before releasing the exhaust gas **28** from the system **10**. For example, as discussed above, the exhaust gas **28** may include unburned CH₄, oxygen (O₂), as well as other undesirable gases such as nitrogen oxides (NO_x), carbon monoxide (CO), carbon

dioxide (CO₂), nitrous oxide (NO), dinitrous oxide (N₂O) and other combustion by-products that may need to be removed prior to release of the exhaust gas **28** from the system **10**. In certain embodiments, the exhaust gas **28** may include between approximately 100 parts per million volume (ppmv) to approximately 5,000 ppmv of CH₄, and more specifically between 200 and 3500 ppmv and even more specifically between 400 and 2500 ppmv of CH₄. However, it has now been recognized that a reduction in methane emissions levels (typically in the range of a 70-90% reduction) is needed to meet certain operating standards. For example, it is desirable that the level of CH₄ in exhaust gases released from natural gas operated systems be less than approximately 150 to 200 ppmv. Therefore, the exhaust gas **28** is has to be treated in the exhaust gas emissions abatement system **14** in order to reduce and to a very large extent substantially remove the unburned CH₄ and other combustion by-products from the exhaust gas **28** before releasing the exhaust gas **28** from the system **10**. For example, in operation, the exhaust gas emissions abatement system **14** disclosed herein first treats the exhaust gas **28** in a guard bed **36** to convert, capture, and to substantially remove the MOC catalyst poisons (such as, SO₂, Zn, P, Ca, Si, ash, and others), thereby generating a treated intermediate exhaust gas **42**. Following removal of the catalyst poisons, the treated intermediate exhaust gas **42** is fed to MOC bed **40**, which oxidizes and substantially reduces the CH₄ level in the exhaust gas **28**, **42** prior to releasing it from the system **10**.

[0033] As discussed above, one technique for removing CH₄ from the exhaust gas **28** is catalytic oxidation of CH₄ over the MOC. The MOC converts CH₄ via oxidation in the presence and with the participation of O₂ into CO₂ and water (H₂O). The composition of the MOC generally includes at least one noble metal oxide supported on porous inorganic

oxide support. More specifically, the chemical composition of the MOC may include: (i) noble metal oxides of platinum (Pt), palladium (Pd), silver (Ag), iridium (Ir), ruthenium (Ru), rhodium (Rh), osmium (Os) and gold (Au) and combinations thereof, (ii) some base metals (Ba, Cs, etc.), (iii) rare earth elements (Ce, Y, La, Nd, etc.), (iv) small quantities of other elements as dopant or promoters and (v) various porous inorganic oxides as supports (for example, aluminum oxide, titanium oxide, zirconium oxide, cobalt oxide, rare earth oxides, etc.) and mixtures thereof.

[0034] Catalytic activity and overall catalyst life of Pd- and other noble metal based MOCs is adversely affected by various chemical species present in the exhaust gas **28**. For example, chemical species such as SO₂, P, Zn, Ca, Si, ash, among others, adversely affect the catalytic activity of the MOC in methane oxidation and its useful life for methane oxidation/emissions abatement. Therefore, these species act as catalyst poisons for the MOC. The source and the level of the catalyst poisons in the exhaust gas derived from natural gas engines depends on: (i) their level in the engine's fuel source, i.e. their levels in natural gas fuel or natural gas and diesel fuels, lubricating oil and (ii) on the fuel and lubrication oil consumption rates. Certain catalyst poisons (such as, for example, S) are present in the fuel or fuels **18**, and other catalyst poisons (such as P, Zn, Ca, etc. in addition to S) are present in the lubricating oil. With respect to sulfur, the total sulfur level in LNG gas is generally very low (e.g., less than approximately 1 ppmv), and in CNG and pipeline NG the total sulfur level is generally less than approximately 5 ppmv. The sulfur level in the diesel pilot is approximately between 0.1 to 0.5 %wt when conforming to the sulfur level regulations. The sulfur level in lubricating oils is in the range of from approximately 0.2 %wt up to approximately 2 %wt. Therefore, the main source of sulfur in exhaust gases,

such as the exhaust gas **28**, is from the fuel and the lubricating oil for CNG fueled engines, and the lubricating oil for LNG fueled engines.

[0035] To mitigate the effects of the catalyst poisons on the MOC, the exhaust gas emissions abatement system **14** includes a dual bed methane abatement unit **30** having a catalyst poison capturing guard bed **36**, hereinafter “guard bed,” positioned upstream of a MOC bed **40**. In the illustrated embodiment, the guard bed **36** and the MOC bed **40** are housed in a single methane abatement unit. However, in certain embodiments, the guard bed **36** and the MOC bed **40** may be in separate housings. The guard bed **36** and MOC bed **40** are connected via appropriate hardware (such as for example, piping, valve, flanges) that directs and feeds the intermediate exhaust gas **42** from the guard bed **36** to the MOC bed **40**. The guard bed **36** may be positioned on top or on the bottom of the MOC bed **40** in the methane abatement unit **30** depending on the direction of the flow direction of exhaust gas **28**. For example, in embodiments in which the exhaust gas **28** flows in a direction from top to bottom of the methane abatement unit **30**, the guard bed **36** is positioned above the MOC bed **40** such that the exhaust gas **28** flows through the guard bed **36** before flowing through the MOC bed **40**. In embodiments in which the exhaust gas **28** flows in a direction from bottom to top of the methane abatement unit **30**, the guard bed **36** is positioned below the MOC bed **40**. In other embodiments, the guard bed **36** is horizontally positioned adjacent to the MOC bed **40**. The methane abatement unit **30** may also be retrofitted into existing systems.

[0036] The guard bed **36** includes one or more layers of one or more MOC poisons capture components **46** that convert, capture, and remove the catalyst poison(s) from the exhaust gas **28** and, in the process, generate the intermediate exhaust gas **42** having

substantially eliminated or significantly reduced amount of the catalytic poison(s) compared to the exhaust gas **28** (e.g., non-treated exhaust gas). In accordance with embodiments of the present disclosure, the guard bed **36** may remove between approximately 50% to approximately 100% of the catalyst poisons from the exhaust gas

5 **28**. For example, the guard bed **36** may remove 50%, 60%, 70%, 75%, 80%, 90%, or 100% of the catalyst poisons. The one or more layers and components **46** that may be used to capture and remove the catalyst poisons from the exhaust gas **28** include but are not limited to transition metal (e.g., manganese (Mn), vanadium (V), copper (Cu)) oxides supported on or co-mingled with various high (e.g., greater than approximately 0.2 cc/g) or low (e.g.,

10 less than approximately 0.2 cc/g) porosity inorganic oxides such as aluminum oxides, titanium oxide, cerium oxide and calcium or magnesium carbonates or oxides, or mixtures of oxides and carbonates materials. The one or more components **46** of the guard bed **36** may catalytically react with and convert at least a portion of the catalyst poisons in the exhaust gas **28** into more reactive species that react and are captured by other components

15 of the guard bed **36** or are converted into chemical species that do not have a significant deleterious effect on the MOC and its catalytic performance, thereby generating the intermediate exhaust gas **42**. The intermediate exhaust gas **42** then exits the guard bed **36** and flows into the MOC bed **40** and where it is subjected to the MOC in the methane abatement unit **30**. In certain embodiments, the one or more layers and components **46** of

20 the guard bed **36** may chemically react with the catalyst poisons in the exhaust gas **28** to produce stable chemical species that remain on the surface of the guard bed **36**. In another embodiment, the one or more components **46** of the guard bed **36** may physically adsorb the catalysts poisons in the exhaust gas **28**, thereby trapping them in the guard bed **36**. The

intermediate exhaust gas **42** output from the guard bed **36** is fed to the MOC bed **40** where the CH₄ in the intermediate exhaust gas stream **42** is oxidized, i.e. converted to CO₂ and H₂O to generate a treated exhaust gas **48** that has less than between approximately 150-500 ppmv of CH₄. In this way, the exhaust gas emission abatement system **14** disclosed herein
5 generates a treated exhaust gas that may meet emission regulatory standards and be suitable for release from the system **10**.

[0037] As discussed above, the guard bed **36** removes the catalyst poisons from the exhaust gas **28** to mitigate poisoning of the MOC in the MOC bed **40**. The guard bed **36** may include a single layer of one or more components **46** or multi-layers of multi
10 components **46**. The single or multi components **46** in each layer convert or capture one or more catalyst poisons present in the exhaust gas.

[0038] FIG. 2 is a block diagram of the methane abatement unit **30** having a multi-layer guard bed **50** positioned upstream of the MOC bed **40**, in accordance with an embodiment of the present disclosure. In the illustrated embodiment, the multi-layer guard
15 bed **50** includes a first layer **54** having a first catalyst poisons conversion and/or capture component **56** (MOC poisons capture component) and a second layer **58** having a second catalyst poison conversion and/or capture component **60** (MOC poisons capture component) downstream of the first layer **54**. The catalyst poisons conversion and/or capture components **56**, **60** in each respective layer **54**, **58** may include one or more
20 chemical species (elements, metal hydroxides or oxides) that are selected and configured in such a way so as to convert and/or capture/trap and, at least in part, remove catalyst poisons from the exhaust gas **28**. The layers **54**, **58** are arranged in a sequential or stacked configuration. As should be noted, certain embodiments of the present disclosure include

a single layer guard bed rather than the multi-layer guard bed **50**. The single layer guard bed includes the component **56**, the component **60**, or a mixture of both.

[0039] As discussed above, the components **56**, **60** remove the catalyst poisons from the exhaust gas **28**. For example, the components **56**, **60** may include chemical species that readily react with SO₂ to oxidize the SO₂ (in the presence of oxygen) in the exhaust gas, thereby forming SO₃. By converting SO₂ into SO₃, the sulfur species become more reactive with the surface of the components **56**, **60**. As such the ability/degree of utilization of the components **56**, **60** for removal of the sulfur species from the exhaust gas (e.g., the exhaust gas **28**) is improved compared to systems that do not include the components **56**, **60**. For example, the components **56**, **60** facilitate the formation of a stable and inert metal sulfates, for example manganese sulfate (MnSO₄), aluminum sulfate (Al₂(SO₄)₃), calcium sulfate (CaSO₄), magnesium sulfate (MgSO₄), etc. These sulfates are stable and, once formed, they remain in the guard bed **50**. Consequently, the active centers on the noble metal oxide phase, and more specifically, the oxygen vacancies within this phase of the MOC in the MOC bed **36** remain unaffected by sulfur species. Therefore, the oxygen vacancies within the noble metal oxide phase of the MOC are available to catalytically oxidize the CH₄ in the exhaust gas **28**. In addition to chemical species that convert SO₂ into SO₃ and sulfates, the components **56**, **60** include other chemical species that react or adsorb and/or form stable complexes with other catalyst poisons in exhaust gas **28** such as Zn, Ca, Mg, P, ash, among others. That is, the components **56**, **60** react and convert or adsorb and essentially trap these other catalysts poisons within the guard bed **50** such that the catalyst poisons do not exit the guard bed **50** along with the intermediate exhaust gas **42**.

[0040] In accordance with the present disclosure, catalyst poison capturing components that may be used to remove catalyst poisons in the exhaust gas (e.g., the exhaust gas **28**) include, but are not limited to, transition metal (manganese (Mn), vanadium (V), copper (Cu)) and others) oxides, lime (CaO), calcium magnesium oxide (CaMgO₂), dolomite (CaMg(CO₃)₂), or mixtures thereof, metal oxides (e.g., magnesium oxide (MgO), aluminum oxide (Al₂O₃)), and combinations thereof. Some of the transition metal oxide sites react with the SO₂ and the O₂ in the exhaust gas **28** to produce SO₃. The resultant SO₃ and residual O₂ also react with the remaining available transition metal oxide sites to produce the respective transition metal sulfates. In addition, the SO₃ may readily react with the porous inorganic oxide such as for example, aluminum oxide and or dolomite-derived material in the guard bed to form stable aluminum and calcium or calcium and/or magnesium sulfates. These stable sulfates are inert and remain within the layer **54**, **58** and components **56**, **60** of the guard bed **50**. Therefore, in this way, sulfur species that are present in the exhaust gas **28** are converted into stable sulfates and are no longer able to exert an undesirable effect on the active centers on the noble metal oxide phase(s) of the MOC. As such, the active centers of the noble metal oxide phase(s) of the MOC remain fully available for methane oxidation during operation of the system **10**.

[0041] High porosity materials such as Al₂O₃ and other inorganic oxide components of the guard bed **50** are also able to react with or adsorb, and essentially remove, other catalyst poisons present in exhaust gas, such as P, Zn, Ca, Mg, Si, ash, etc. that may not be removed by low porosity (water pore volume less than approximately 0.2 cubic centimeter/gram (cc/g)) materials such as dolomite-derived materials. The porous materials may react and bind or adsorb the aforementioned catalyst poisons, thereby

trapping them in the guard bed and removing them from the exhaust gas. In certain embodiments, the component **56** in the first layer **54** of the guard bed **50** is a transition metal oxide or any other suitable metal oxide deposited on or co-mingled with a high porosity (water pore volume greater than approximately 0.2 cc/g) material such as Al_2O_3 and the component **60** in the second layer **58** of the guard bed **50** is a transition metal oxide or other suitable oxide? deposited on or co-mingled with relatively low porosity (water pore volume of less than approximately 0.2 cc/g) dolomite-derived material. The first layer **54** of the guard bed **50** may be a section that converts and/or traps a portion of the catalyst poisons in the exhaust gas **28** before the exhaust gas flows into the second layer **58** of the guard bed **50** for final trapping of the remaining poisons. For example, the first layer **54** may remove between approximately 5% and 90% or between 30 and 70 % of the catalyst poisons in the exhaust gas **28**. In certain embodiments, the first layer **54** may be selective for certain catalyst poisons and the second layer **58** towards other catalyst poisons. Specifically, the component **56** in the first layer **54** may be selective for oxidation of SO_2 to SO_3 and for certain elements and ash and the component **60** in the second layer **58** may complete the oxidation of SO_2 to SO_3 and be more selective for binding these sulfur species and forming sulfates. In accordance with an embodiment of the present disclosure, the components **56**, **60** may include transition metal (e.g., Mn, V, Cu) oxides that are deposited on or co-mingled with the high porosity (water pore volume greater than approximately 0.2 cc/g) metal oxide and the relatively low porosity (water pore volume less than approximately 0.2 cc/g) dolomite-derived material. Furthermore, the level of transition metal in the respective components **56**, **60** is between approximately 1 % weight (%wt) and 25 %wt and more specifically between approximately 5 %wt and 15 %wt.

[0042] FIG. 3 illustrates an embodiment of the multi-layer guard bed 50 that may be used to capture and remove catalyst poisons from the exhaust gas 28, in accordance with the present disclosure. As illustrated in FIG. 3 the multi-layer guard bed 50 has a total length 62 that extends from an upstream end 64 to a downstream end 68, a width 70 (i.e., thickness) that is substantially orthogonal to the length 62 and extends between a first side 72 and a second side 74 of the guard bed 36, and a height 78 that is substantially orthogonal to the length 62 and width 70 and extends between a top side 80 and a bottom side 82 of the multi-layer guard bed 50. The length 62, width 70, and height 78 define a volume 86 (e.g., total guard bed volume) of the multi-layer guard bed 50. While in the illustrated embodiment, the multi-layer guard bed 50 has a rectangular shape, the multi-bed guard bed 50 may have any other geometric shape (e.g., square, cylindrical, oval, etc.). As should be appreciated, the layers 54, 58 and components 56, 60 in the multi-layer guard bed 50 may be arranged in a fixed or a moving or movable bed configuration. The latter might allow for replacement or replenishment of layers 54, 58 saturated with poisons without interruption of the engine and exhaust gas emissions abatement system operation.

[0043] As illustrated in FIG. 3, the volume 86 is divided into the first layer 54 and the second layer 58. The volume 86 within the first layer 54 includes the first poisons capturing component 56 and the second layer 58 includes the second poisons capturing component 60. The first layer 54 extends along a first portion 90 of the length 62 such that the first layer 54 occupies between approximately 1% and approximately 99% of the total guard bed volume 86. Similarly, the second layer 58 extends along a second portion 92 of the length 62 such that the second layer 58 occupies between approximately 1% and approximately 99% of the volume 86. Dimensions of the portions 90, 92 may be the same

or different. For example, the layers **54**, **58** may be equally distributed along the length **62** of the multi-layer guard bed **50**. As such, each portion **90**, **92** of the respective layer **54**, **58** is approximately 50% of the total length **62** of the multi-layer guard bed **50**, and the respective poison capturing components **56**, **60**, occupy approximately 50% of the total guard bed volume **86**. In other embodiments, the dimensions of the portion **90** of the first layer **54** may be more or less than the dimensions of the portion **92** of the second layer **58**. Therefore, the first poisons capturing component **56** occupies more or less of the volume **86** compared to the second poisons capturing component **60**. For example, the first poison capturing component **56** may occupy between approximately 1% and approximately 49% of the volume **86** and the second poison capturing component **60** may occupy between approximately 51% and approximately 99% of the volume **86**, and vice versa.

[0044] In certain embodiments, the first poison capturing component **56** in the first layer **54** may partially oxidize the SO_2 to SO_3 and partially react and capture the SO_3 in the form of sulfates while at the same time react with, adsorb, capture, and remove the non-sulfur catalyst poisons. The second poisons capturing component **60** in the second layer **58** may primarily complete the oxidation and capture remaining unconverted SO_3 in the first layer **54** (i.e. removing the remaining sulfur poisons) while also capture and remove any remaining non-sulfur poisons that may have passed through the first layer **54**. For example, in the embodiment illustrated in **FIG. 3**, the first poisons capturing component **56** is selected in such a way so that SO_2 is partially oxidized to SO_3 and captured in the form of sulfates. The layer **54** also largely reacts with, adsorbs or captures the non-sulfur catalyst poisons such as Zn, P, Ca, Mg, Si, ash and others. The second poisons capturing component **60** in the second guard bed layer **58** is selected in such a way so that to complete

the conversion of any SO₂ that might have passed through the first bed **58** into SO₃ and to react and capture it (i.e. all remaining of sulfur poisons) as sulfates while simultaneously completing the capture of certain remaining non-sulfur poisons that might have passed through the first guard bed layer **54**.

- 5 **[0045]** Therefore, to remove the sulfur and catalysts poisons in the manner discussed above, the first poisons capturing component **56** may include at least one transition metal oxide deposited on or co-mingled with at least one preferably high porosity (water pore volume greater than approximately 0.2 milliliters (mL)/gram (g)) inorganic oxide material such as, but not limited to, aluminum oxide (Al₂O₃), crystalline or amorphous
- 10 aluminosilicate, titanium oxide, cobalt oxide, magnesium oxide, or any other suitable high porosity material or mixtures thereof that may react, convert, adsorb, or otherwise bind, the sulfur and non-sulfur catalyst poisons in the exhaust gas passing through the first layer **54**. In this particular case, the transition metal oxide function provides for the oxidation of SO₂ to SO₃ and its partial capturing as sulfates, whereas the high porosity inorganic oxide
- 15 material provides the necessary high surface area and chemical functionality needed to bind, adsorb and/or capture the sulfur and non-sulfur poisons. The second poisons capturing component **60** includes at least one transition metal oxide deposited on or co-mingled with relatively low porosity (water pore volume less than approximately 0.2 mL/g) but high sulfur uptake capacity material selected from but not limited to calcium
- 20 oxide (lime), calcium magnesium oxide, calcium carbonate, calcium magnesium carbonate (dolomite) and mixtures thereof. For the second poisons capturing component **60**, the transition metal oxide function also converts any remaining SO₂ in the exhaust gas to SO₃ and partially binds the SO₃ in the form of transition metal sulfates. The relatively low

porosity (for example, dolomite-derived, <0.2 mL/g) material completes the capturing of SO₃ by forming sulfates while helping to complete the removal of the remaining non-sulfur poisons.

[0046] In one embodiment, the component **56**, and/or the component **60**, may be prepared by impregnating the high porosity (such as, for example, Al₂O₃) and low porosity (for example, dolomite-derived) inorganic materials with a suitable transition metal precursor to achieve a final transition metal concentration in the respective poisons capturing components **58**, **60** of approximately 1% to 25%. More preferably, the impregnation could be carried out to achieve a transition metal concentration in the overall poisons capturing components **58**, **60** of approximately 5 to 20 %wt. By impregnating the high and low porosity materials of the components **56**, **60** with the transition metal precursor, the efficiency of the poisons capturing components **56**, **60** for oxidation and removal of SO₂ is increased compared to materials/components not impregnated with the transition metal precursor. In other embodiments, the transition metal precursor could be added during the stage of synthesis of the high or relatively low porosity materials in the component **56**, **60** or co-mingled with the component **56**, **60** during preparation via co-mulling (physical mixing), which may be followed by shaping of the component **56**, **60**. The transition metal (M) could be added in the above steps in the form of a transition metal precursor (such as for example M_x(NO₃)_y, M_xCl_y, etc.), transition metal hydroxide (M(OH)_x) or transition metal oxide (M_xO_y). In all instances, the transition metal in the final poisons capturing components **56**, **60** is in the form of a transition metal oxide.

[0047] In certain embodiments, the volume **86** of the guard bed may be a single layer rather than a multi-layer, such as in the multi-layer guard bed 50. For example, the single-

layer guard bed may include comprising a physical mixture of the first poisons capturing component **56** and the second poisons capturing component **60**. For example, **FIG. 4** illustrates an embodiment of a single-layer guard bed **96** that may be used in the methane abatement unit **30** to remove catalyst poisons from the exhaust gas **28**. In the illustrated
5 embodiment, the volume **86** of the single-layer guard bed **96** is uniformly packed with a capture material **98** that is a physical mixture of the poisons capturing components **56**, **60**. A ratio of the component **56**, **60** in the capture material **98** may be 1:1, 1:2, 1:3, 1:4, 2:3, 2:1, 3:1, 4:1, 3:2 or any other suitable ratio. In certain embodiments, the mixture **98** includes individual pellets of the first poisons capturing component **56** and individual
10 pellets of the second poisons capturing component **60**. In other embodiments, the capture material **98** includes shaped particles (for example, pellets) of a capture component formed by co-extruding a physical mixture of both components **56**, **60**.

[0048] By incorporating the guard bed **50**, **96** into the methane abatement unit **30**, the catalytic performance in methane oxidation and useful life of the MOC may be
15 significantly improved/extended. For example, returning to **FIG. 2**, in operation, the methane abatement unit **30** receives the exhaust gas **28** output by a natural gas engine (e.g., the natural gas engine **12**). While in the methane abatement unit **30**, the exhaust gas **28** flows into the guard bed **50**, **96** and directly contacts the poisons capture components **56**, **60**, **98**. The components **56**, **60**, **98** remove the catalyst poisons in the exhaust gas **28** by
20 reacting, converting, adsorbing, or otherwise capturing the catalyst poisons, and in the process generating the intermediate exhaust gas **42**. Following generation of the intermediate exhaust gas **42**, the guard bed **50**, **96** directs the intermediate exhaust gas **42** to the MOC bed **40**, which includes a methane oxidation catalyst (MOC) **94**.

[0049] As discussed above, the MOC 94 may be any noble metal oxide catalyst. For example, the MOC 94 may be PdO-based catalyst on an inorganic oxide (e.g., zirconium oxide) containing support. In the MOC bed 40, the intermediate exhaust gas 42 directly contacts the MOC 94. The MOC 94 includes at least one active noble metal oxide phase that reacts with CH₄ in the intermediate exhaust gas 42 and oxidizes CH₄ due, in part, to the presence of oxygen in the exhaust gas to form CO₂ and H₂O. Because the guard bed 50, 96 removes the catalyst poisons from the exhaust gas 28, the active noble metal oxide phase of the MOC 94 is not adversely affected by the poisons and is, therefore, fully available to oxidize/abate the CH₄ in the intermediate gas 42. The above enables the MOC 94 to fully exert its methane oxidation activity and to sustain it for a significantly long period of time (e.g., tens of thousands of hours on stream) compared to MOC that are not positioned downstream of the guard bed 50, 96. As such, the CH₄ levels in the treated exhaust gas 48 generated by the methane abatement unit 30 may be approximately 150-200 ppmv. CH₄ levels of approximately 150-200 ppmv are at or below permissible CH₄ emission levels.

EXAMPLES

[0050] Set forth below are experiments illustrating the performance of the guard bed disclosed herein. Each of the experiments below were generally run using various powder guard bed formulations that were intentionally poisoned with SO₂ or aged positioned upstream of a MOC bed. The MOC formulation used throughout the experiments was as follows: (Pd (4 %wt) Pt (0.5 %wt) Rh (0.125 %wt) on a zirconium (ZrO₂) support. Each powder guard bed was prepared using any suitable technique known in the art to yield a

desired chemical composition, as shown in Table 1. For a reference, performance tests for the MOC were carried out without a guard bed (EXAMPLES 1 and 15).

[0051] The experiments were run in a high throughput powder catalyst testing unit. Each reactor of the high throughput powder catalyst testing unit was loaded such that a ratio of loaded guard bed/MOC was 50/50 vol%. The ability of the powder guard bed to remove catalyst poisons was evaluated in each respective powder guard bed/MOC sample by comparing the performance (or ability) of the MOC positioned downstream of each respective powder guard bed to oxidize or convert methane present in a model (e.g., mimicking) exhaust gas feed composition. To compare the catalytic activity of the various powder guard beds/MOC samples a temperature requirement for 50 % methane conversion (T_{50CH_4}) obtained during the performance test was determined (See Table 1). In all instances, except for EXAMPLE 1, the performance tests were run in 2 stages. In the first stage (EXAMPLES 2-17), the powder guard bed/MOC samples were placed in a high throughput SO_2 aging test rig and subjected to SO_2 aging for a duration of 24 hrs using gas feed containing 5 parts per million (ppm) SO_2 , 500 ppm CH_4 , and 10% vol H_2O , 10,000 h⁻¹ Gas Hourly Space Velocity (GHSV) calculated by dividing volumetric gas flow in L/hr by the volume of catalyst in L, and an inlet gas temperature of 470 °C. Following the SO_2 aging, the powder guard bed/MOC samples were removed from the SO_2 test rig, and reloaded into a “clean” high throughput test rig and tested using exhaust gas mimicking feed containing 2000 ppm CH_4 , 1000 ppm CO, 7.5% vol. CO_2 , 6% vol. O_2 , 150 ppm NO, and 15% H_2O . As used herein, a “clean” high throughput test rig is intended to denote a high throughput test rig that is devoid of sulfur. In the second stage of testing, the performance tests were run without the addition of SO_2 to the gas feed. The powder guard

bed/MOC sample of EXAMPLE 1 was not subjected to SO₂ aging but rather subjected directly to the second (clean, devoid of SO₂ in feed) stage of testing.

Table 1. Methane Oxidation Activity (T_{50CH4}) for MOC*

EXAMPLE#	GUARD COMPOSITION	BED	T _{50CH4} (°C)	SO ₂ - AGED
1	NONE		391	NO
2	Mn(4)/CaMgO ₂ -Al ₂ O ₃		392	YES
3	Cu(10)/CaMgO ₂		394	YES
4	CaMgO ₂		394	YES
5	Ce(2)Cu(4)/CaMgO ₂		395	YES
6	CaO		395	YES
7	Ce(2)Cu(4)/CaMg(CO ₃) ₂ Yes		396	YES
8	K(8)MgO-Al ₂ O ₃		397	YES
9	CaMgO ₂ -Al ₂ O ₃		398	YES
10	Ca(10)/Al ₂ O ₃		401	YES
11	Ce(2)Cu(4)/MgO-Al ₂ O ₃		407	YES
12	CuO/ZnO/Al ₂ O ₃		415	YES
13	Mn(6)/Al ₂ O ₃		428	YES
14	MgO-Al ₂ O ₃		442	YES
15	NONE		458	YES
16	Al ₂ O ₃		462	YES
17	Ni/Al ₂ O ₃		462	YES

*The numbers in parentheses represent the %wt concentration of the respective element in the final guard bed formulation

- 5 **[0052]** Analysis of the data in Table 1 indicates that, following SO₂ aging, the powder guard bed/MOC samples containing calcium-magnesium (i.e., dolomite)-derived and calcium oxide (lime)-based guard bed formulations (e.g., EXAMPLES. 2-6) exhibited the lowest T_{50CH4} values (392-395°C). The T_{50CH4} values observed in EXAMPLES 2-6 are at desired levels indicating that the dolomite-derived and lime-based guard bed
- 10 formulations have the best methane oxidation activity compared to the other powder guard bed/MOC combinations tested. Furthermore, certain SO₂ aged powder guard bed/MOC

samples from EXAMPLES 2-6 provided very similar catalytic activity (i.e. T_{50CH_4} values) to the reference/control MOC that was not subjected to SO_2 aging ($T_{50CH_4}=391^\circ C$). It should be noted that, the MOC sample which was subjected to SO_2 aging without the guard bed (EXAMPLE 15) exhibited significantly lower methane oxidation activity as evidenced by its T_{50CH_4} value of $458^\circ C$, which is $67^\circ C$ higher than the MOC that was not subjected to SO_2 aging (EXAMPLE 1). Therefore, as determined from the data in Table 1, powder guard beds having calcium magnesium or calcium formulations effectively remove the SO_2 MOC catalyst poison that, otherwise, would have adversely affected and significantly decreased the catalytic activity and activity stability of the MOC. It should be noted that, the guard bed formulation having a transition metal oxide deposited on a support containing calcium and magnesium oxide (e.g., $CaMgO_2$) along with Al_2O_3 (e.g., EXAMPLE 2), afforded the best SO_2 capturing performance compared to the other powder guard bed/MOC samples tested. This is evidenced by the lowest T_{50CH_4} value ($392^\circ C$), i.e. highest methane oxidation activity exhibited by this guard bed formulation (EXAMPLE 2) relative to all SO_2 aged powder guard bed/MOC samples tested. Notably, the specific transition metal oxide and $CaMgO_2$ and Al_2O_3 powder guard bed formulation of EXAMPLE 2 afforded, following the SO_2 aging, essentially the same T_{50CH_4} value, i.e. methane oxidation activity, as the reference MOC sample (EXAMPLE 1) which was not aged with SO_2 and tested in the absence of a guard bed (the most active sample, $T_{50CH_4}=391^\circ C$).

[0053] The transition metal (Mn or Cu) oxide in the guard bed formulation, when in the presence of oxygen, provides for rapid oxidation of SO_2 to SO_3 . The calcium magnesium-based support in the guard bed formulation primarily reacts with and captures the SO_3 in

the form of sulfates, whereas the Al_2O_3 primarily provides higher surface area and chemical functionality that is beneficial for adsorbing, reacting or capturing some of the other non-sulfur poisons that might be present in the exhaust gas. In addition, the Al_2O_3 could also contribute, at least in part, to further removal of the sulfur containing poisons by reacting and converting them to aluminum sulfates. Examples 2-6 and their respective data clearly illustrate the beneficial effect of having the transition metal oxide, calcium, magnesium, and alumina in guard bed formulation disclosed herein upstream of the MOC bed. For example, the disclosed transition metal oxide, calcium, magnesium, and alumina guard bed formulation is effective in removing the S containing catalyst poisons from exhaust gas derived from natural gas burning engines thus allowing the MOC catalyst placed downstream of it to fully exert and maintain its methane oxidation activity and performance stability. Accordingly, the transition metal oxide, calcium, magnesium, and alumina guard bed formulations of the present disclosure are suitable for use in methane emissions abatement system to abate unburned methane from natural gas fueled engines in a stationary and a transport service.

Dual-layer Guard Bed

[0054] As discussed above, the guard bed of the present disclosure may have multiple layers of different guard bed formulations. A dual-layer guard bed formulation was prepared and tested for removal of sulfur and other catalysts poisons (EXAMPLE 18). The first layer of the dual-layer guard bed includes a transition metal oxide and Al_2O_3 component. The second layer of the dual-layer guard bed includes a transition metal oxide and calcium magnesium carbonate (dolomite)-derived component. These two layers and

components are arranged in a stacked configuration (one after another) and positioned upstream of the MOC bed.

Preparation of the First Layer- Al_2O_3 Component of the Guard Bed:

[0055] The first layer of the dual-layer guard bed may be prepared by impregnating shaped
5 (extruded) alumina aggregates (e.g., alumina pellets) with an aqueous solution of a transition metal precursor. The transition metal precursor may be added to an alumina aggregate formulation prior to or after extrusion. For example, the transition metal precursor may be added to an extrusion mix used to prepare the alumina pellets. The extrusion mix is prepared by mixing alumina (or aluminum hydroxide) powder and a
10 peptizing agent. Alternatively, an aqueous solution of the transition metal precursor may be added to prepared alumina pellets (e.g., extrudate) via any one of the impregnation methods known in the art. For example, the alumina pellets may be impregnated via pore volume impregnation or by circulating impregnation solution. The alumina pellets may be any suitable geometric shape. By way of non-limiting example, the alumina pellets may be
15 cylindrical, polylobal (e.g., trilobed), spheres, rings, or tablets. Dimensions of the alumina pellets range from between approximately 1.2 and 10 mm in diameter and approximately 4 and 10 mm in length.

[0056] The Al_2O_3 component/support used in EXAMPLE 18 was prepared according to the method described in US Patent 4,579,729. Briefly, an extrusion mix (for the support)
20 was prepared by placing 654 g of wide pore alumina powder (LOI=23.5%w) in a muller mixer bowl and, while running the muller mixer bowl, a solution of nitric acid peptizing agent was added, thereby forming an alumina/peptizing agent solution mix. The

alumina/peptizing agent solution mix was mulled in the muller for approximately 15 minutes to allow the peptizing agent to react with the wide pore alumina powder. Alternatively, an inorganic hydroxide sol (e.g., aluminum hydroxide sol) binder may be mixed with the wide pore alumina powder for between approximately 10 to 30 mins to allow for a peptization or binding of the wide pore alumina powder. Extrusion aids, such as for example, citric acid, Superfloc, and/or Methocell, among others, may also be added to the alumina/peptizing agent solution mix to improve the ease of the extrusion and partially, when needed, to generate additional porosity.

[0057] Following addition of one or more extrusion aids, approximately 130 g of DI water was added to the muller and the muller was restarted. Once addition of the DI water was completed, the extrusion mix was mulled for approximately 15 minutes, transferred to a stainless-steel tray, and extruded using a die plate into trilobe (TL) pellet strands having a diameter of approximately 2.5 mm. The TL pellet strands were collected, transferred to a drying convection oven, and dried at 120 °C overnight. Once dry, the TL pellet strands were crushed and sieved to yield TL pellets of approximately 4 to 6 mm in length. The dried and sized TL pellet strands were calcined in 40L/hr of a dry air flow at a heating rate of 2°C/min to 600°C and held at 600°C for 6 hrs.

[0058] Following calcination, the TL pellet strands were impregnated using the pore volume impregnation method to target a 10% concentration of Mn on the TL pellet strands. The impregnation solution was prepared by dissolving approximately 6460 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4.85\text{H}_2\text{O}$ with 6914 mL of DI water to yield a manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) solution having between approximately 25 wt.% and approximately 75 wt. % $\text{Mn}(\text{NO}_3)_2$. The volume of the prepared impregnation solution was then topped

with additional DI water to adjust total volume needed to satisfy the pore volume of the extrudate quantity to be impregnated (8680 mL). For example, in the pore volume impregnation method, the volume of the impregnation solution used is substantially the same as the pore volume TL pellet strands. In this particular example, the total water pore
5 volume of the Al_2O_3 TL pellet strands was 0.868 mL/g. Therefore, the volume of the $\text{Mn}(\text{NO}_3)_2$ impregnation solution was adjusted to 8680 mL and used to impregnate 10 kg of the Al_2O_3 TL pellet strands in a rotating impregnation vessel. While rotating the impregnation vessel, a portion of the $\text{Mn}(\text{NO}_3)_2$ impregnating solution was added in a small stream-like mode to the TL pellet strands in the vessel. The TL pellet strands and the
10 $\text{Mn}(\text{NO}_3)_2$ impregnation solution were allowed to homogenize for few minutes. Following homogenization of the TL pellet strands and the portion of the $\text{Mn}(\text{NO}_3)_2$ impregnation solution the remaining portion of the $\text{Mn}(\text{NO}_3)_2$ impregnation solution was slowly added to the rotating impregnation vessel, thereby forming the impregnated pellets.

[0059] The impregnated pellets were allowed to tumble in the rotating impregnator for
15 approximately 10 minutes, after which the impregnated pellets were transferred into trays and allowed to air dry overnight followed by drying in a 40L/hr flow of dry air at 120 °C for 12 hrs. The dried impregnated pellets were calcined using a heating rate of 2°C/min to 600 °C and holding at 600 °C for 6 hrs.

Preparation of the Second Layer-Second Component of the Guard Bed:

20 [0060] The second layer of the dual-layer guard bed may be prepared in a manner similar to the first layer. As discussed above, the second layer is positioned downstream of the first layer in the dual-layer guard bed. The second layer includes a transition metal

oxide and dolomite-derived component prepared by mixing 25 kg of dolomite ($\text{CaMg}(\text{CO}_3)_2$) powder particles having an average particle size of between approximately 5 microns (μm) and approximately 15 μm and 6476.5 g of LUDOX AS-40 silica sol binder having 40 %wt silica solids content in a mix muller to form an extrusion mix. The LUDOX AS-40 silica sol was used as a binder to bind individual dolomite powder particles together and to help shape the dolomite particles into shaped aggregates (e.g., pellets, spheres, rings, tablets, etc.) of the desired diameter via extrusion.

[0061] The extrusion mix was muller in the mix muller for approximately 10 minutes. While in the mix muller, approximately 294 g of Methocel was added to the extrusion mix at approximately 2 minutes, followed by approximately 126.5 g of Superfloc at approximately 6 minutes of from the start of mulling. The extrusion mix was muller for an additional 10 minutes and the resultant mixture was extruded into 2.5 mm diameter TL extrudate strands. The TL extrudate strands were air dried at ambient temperature overnight and subsequently dried in a convection drying oven overnight at 100 °C. The dried TL extrudate strands were crushed to form pellets having a length of between approximately 4 mm to approximately 8 mm and calcined in a 40 L/hr flow of dry air using 2°C/min heating rate to and holding at 600 °C for 6 hrs, thereby forming a calcined dolomite-derived TL extrudate. The calcined dolomite-derived TL extrudate was subjected to impregnation with a transition metal precursor to form a Mn-impregnated dolomite-derived TL pellets (e.g., the second component) of the dual-layer guard bed. The calcined dolomite-derived TL extrudate was impregnated using the $\text{Mn}(\text{NO}_3)_2$ impregnation solution discussed above with reference to the Al_2O_3 component of the first layer of the dual-layer guard bed. The targeted final concentration of Mn on the dolomite-derived

component was 8 % wt. The Mn-impregnated dolomite-derived TL pellets were air-dried overnight followed by drying in a convection oven at approximately 120 °C for at least 2 hrs. Following drying, the impregnated dolomite-derived TL pellets were subjected to a dry air flow of 40L/hr, heated at a 2 °C/min ramp rate and calcined at 600 °C for approximately 6 hrs.

EXAMPLE 19 – Dual-Layer Guard Bed

[0062] To illustrate the ability of the aforementioned dual-layer guard bed of EXAMPLE 18 to capture sulfur containing and other catalyst poisons from an exhaust gas generated by and output from an engine operated with a LNG as a fuel, the dual-layer guard bed was positioned upstream of a MOC bed and the CH₄ abatement activity of the MOC in the MOC bed was evaluated. For example, the methane conversion measured during this test was used as a measure of the effectiveness of the guard bed to capture the poisons in exhaust gas. The test was done using a 12 L six cylinder LNG fueled, spark ignited engine operating under lean fuel regime. The test was done at a GHSV of approximately 50,000 h⁻¹. The fuel used to operate the natural gas engine was LNG having approximately 98 %volume (%vol) CH₄, 2 %vol C₂₊, and S less than 0.1 ppm. A composition of the exhaust gas generated by the natural gas engine was 1600 ppmv CH₄, 450 ppm CO, 7.3 %vol CO₂, 8.4 %vol O₂, 140 ppmv NO, 12.5 %vol H₂O, and 0.15 ppm SO₂, and a temperature of the exhaust gas existing the natural gas engine was approximately 470 °C. The dual-layer guard bed was loaded with a first (upstream) layer of 1.03 kg of 10% Mn/Al₂O₃ 2.5 mm diameter TL pellets (EXAMPLE 18) and 3.6 kg of 8%w Mn/dolomite 2.5 mm TL pellets (EXAMPLE 18). The MOC was prepared by washcoating of a slurry containing the MOC catalyst components on a 4.16” in diameter by 3.5” long ceramic monolith substrate with

400 cpsi (pore channels per square inch). The composition of the washcoated MOC catalyst was 4%wt Pd, 0.5%wt Pt, 0.125%wt Rh on ZrO₂.

[0063] The results of the above described test of the dual-layer guard bed formulation of EXAMPLE 18 is shown in FIG. 5. FIG. 5 is a plot 100 of percent CH₄ conversion as a function of time in hours. As shown, the data 102 clearly indicates that the dual-layer guard bed/MOC system of the present disclosure maintained 100% CH₄ conversion for the duration of the test. As such, the dual layer guard bed formulation of EXAMPLE 18 used for this test effectively converted, adsorbed, or captured the S and other poisons present in the engine exhaust gas thus allowing the PdO-based MOC to fully exert methane oxidation/abatement activity for the duration of the test.

[0064] FIGS. 6 and 7 are plots 130 and 132 showing the catalyst poisons distribution profiles/concentrations in percent weight (%wt) as a function of guard bed length and the MOC bed length, respectively. The poisons distribution profiles shown in FIGS. 6 and 7 were obtained by chemical composition analysis of spent guard bed and MOC monolith samples taken from the engine test described above using inductively coupled plasma (ICP) techniques. The spent guard bed and MOC monolith samples were taken from different sections along a length of the respective guard bed layers (FIG. 6) and the MOC monolith (FIG. 7). As discussed above, the dual-layer guard bed and the MOC bed were subjected to the exhaust gas stream for a duration of 1000 hrs. Therefore, the dual-layer guard bed formulation and the MOC in the MOC bed were exposed to the catalyst poisons that originated from the LNG fuel and the lubricating oil used for operation of the natural gas engine. As shown in FIG. 6, the Mn/Al₂O₃ component in the first guard bed layer effectively captured and reduced the concentrations of sulfur (S), silicon (Si), and

phosphorus (P) catalyst poisons in the exhaust gas, whereas the Mn/dolomite-derived component of the second guard bed layer captured and reduced remaining concentrations of S and P in the exhaust gas. It should be noted that the Si concentration in the second guard bed layer was not determined because the dolomite-derived pellets were extruded with silica sol as a binder. Therefore, the Si concentration in the second guard bed layer would not be representative of the amount of Si removed from the exhaust gas by the second guard bed layer. Zn is not detected along the dual-layer guard bed length because the amount of Zn is relatively small (under detection limit) as it's distributed on a large surface area of the guard bed.

10 [0065] As shown in **FIG. 7**, the concentrations of catalyst poisons along the length of the MOC monolith bed is very low (< 0.05 %wt.). Specifically, the data shows that the concentration of the S was as low as 0.025 % wt and decreased along the length of the MOC to about 0.01 %wt. In addition, the level of P on the spent MOC was below detectable levels across the length of the MOC bed. The concentration of Si was not

15 determined due to the presence of silica in the MOC monolithic support material. The above catalyst poisons profiles and catalyst performance data demonstrate that the dual-layer guard bed disclosed herein effectively remove the S and non-S containing MOC poisons from the exhaust gas. Consequently, the MOC catalyst may fully exert CH₄ oxidation/conversion and CH₄ emissions abatement activity compared to systems that do

20 not include the disclosed guard bed (see **FIGS. 8 and 9**).

Single-Layer Guard Bed

[0066] In addition to the dual-layer guard bed tests, the CH₄ conversion activity of the MOC was also tested using a single-layer guard bed. The layer of the single-layer guard bed includes a single component such as, for example, transition metal (M)/Al₂O₃ or M/dolomite-derived material. However, in certain embodiments, the layer of the single-layer guard bed includes a physical mixture of two or more components, as discussed in further detail below. The single component of the single-layer guard bed may be prepared by physically mixing Al₂O₃ and Mn/dolomite powder particles of appropriate size, adding a peptizing agent or a binder to prepare an extrusion or shaping mix having the desired shaping consistency, and extruding or otherwise shaping the mix of these particles to produce homogeneously intermixed Al₂O₃ and dolomite-derived aggregates (e.g., pellets, tablets, spheres, or rings). In this particular embodiment, the Al₂O₃ and dolomite-derived particles are chemically bound. The transition metal M (for example, Mn) addition could be accomplished either via transition metal precursor addition during the extrusion mix preparation or during the mix pre-shaping stage. In other embodiments, the transition metal M may be incorporated into the Al₂O₃ and dolomite-derived aggregates via impregnation with a transition metal precursor. In all cases, the extrusion mix have to be peptized with a carefully selected peptizing agent or it will need to be subjected to a binder addition.

[0067] The addition of additives, such as the peptizing agent or binder, to the shaping mix provide for proper binding of the particles and to ensure sufficient structural integrity of the calcined pellets, tablets, rings or spheres. The peptizing agents modify the surface of the particles (e.g., Al₂O₃ or the dolomite-derived material), by making them more reactive, which facilitates binding of the particles with the surface of other particles. Certain peptizing agents may be large or bulky enough (e.g., of a large molecule size, such as citric

acid - $C_6H_8O_7$) to improve not only the surface reactivity (i.e., susceptibility for binding) of the particles, but also to increase the final pore size and porosity of the calcined aggregates. The increase in pore size may be substantial compared to particles treated with peptizing agents of a smaller size (e.g., nitric acid HNO_3). These increased pore size or total porosity
5 of the shaped and calcined aggregates of the single component may provide for better access to their surface by catalyst poisons and react with and or allow for the accommodation of larger amounts of catalyst poisons. By way of non-limiting example, the peptizing agents include nitric acid, acetic acid, citric acid, or any other suitable peptizing agent. In addition to the peptizing agents, other extrusion aids (such as Methocel,
10 Superfloc, etc.) may be added to the shaping or extrusion mix to improve the shaping process. These could also impart additional pore size modifications and total porosity increase.

[0068] In other embodiments, the layer of the single-layer guard bed is a physical mixture of two components. For example, the layer may be a physical mixture of M/Al_2O_3 and
15 M /dolomite-derived components, such as those discussed above with respect to EXAMPLE 18. The physical mixture may be generated by mixing pre-shaped Al_2O_3 particles (as pellets, tablets, rings or spheres) with pre-shaped dolomite-derived particles (as pellets, tablets, rings or spheres). In certain embodiments, the pre-shaped Al_2O_3 and dolomite-derived particles are mixed prior to impregnating with the M precursor. In other
20 embodiments, the pre-shaped Al_2O_3 and dolomite-derived particles are mixed after impregnating with the M precursor. In the physical mixture of the Al_2O_3 and dolomite-derived particles, there is no chemical bonding between the Al_2O_3 - and dolomite-derived components.

EXAMPLES 20 and 21 – Single-Layer Guard Bed

- [0069] The single component used in EXAMPLES 20 and 21 were prepared by adding 654 g of wide pore alumina (LOI=23.5%w) to a muller mixer bowl, starting the muller, and adding a solution of nitric acid (EXAMPLE 20) or acetic acid (EXAMPLE 21) peptizing agent to the muller. The respective peptizing agent solutions were prepared by adding 10.8 g of 69.4 % wt. nitric acid to 687 g of DI water or adding 10.8 g of glacial (100%) acetic acid to 724g of (DI) water. The alumina/peptizing agent solution mix was mulled for 15 minutes to allow the peptizing agent to react with the alumina powder. Following peptizing of the alumina powder, the muller was stopped, a mixture of 500 g of dolomite, 10 g Superfloc, 6 g Methocell and 130 g of 40%wt solids Ludox AS-40 silica sol binder (EXAMPLE 20) or 130 g of DI water (EXAMPLE 21) was added to the muller and the muller was restarted. The resultant 50 %wt Al_2O_3 50 %wt dolomite extrusion mix was mulled for 15 minutes after which it was extruded into 2.5 mm in diameter long Al_2O_3 -dolomite TL pellet strands using a die plate. The Al_2O_3 -dolomite TL pellet strands were dried in a convection oven at 120 °C overnight. After drying, the Al_2O_3 -dolomite TL pellet strands were crushed and sieved to size to Al_2O_3 -dolomite TL pellet strands of approximately 4-6 mm in length. The sized Al_2O_3 -dolomite TL pellet strands were subjected to calcination in a 40 L/hr of a dry air flow using a heating rate of 2 °C/min to 600 °C and holding at 600 °C for 6 hrs.
- [0070] Following calcination, the Al_2O_3 -dolomite TL pellet strands were impregnated via the pore volume impregnation method discussed above with reference to EXAMPLE 18. Briefly, the total water pore volume for calcined Al_2O_3 -dolomite TL pellet strands in EXAMPLE 20 (nitric acid peptizing solution) and in EXAMPLE 21 (acetic acid peptizing

solution) was 0.50 mL/g and 0.55 mL/g, respectively. For impregnation of the Al₂O₃-dolomite TL pellets in EXAMPLE 21, a transition metal impregnation solution was prepared by dissolving 397.3 g of Mn(NO₃)₂·4H₂O with 60-70% total DI water (330 mL) needed to saturate the total pore volume of the amount of extrudate to be impregnated. The volume of the impregnation solution was adjusted with additional DI water to achieve the total volume needed to satisfy the pore volume of the extrudate quantity to be impregnated (550mL). Approximately 1 kg of the calcined Al₂O₃-dolomite TL pellets from EXAMPLE 21 was placed into a rotating impregnation vessel. While rotating the vessel, approximately half of the Mn(NO₃)₂ impregnating solution was added in a small stream like mode to the Al₂O₃-dolomite TL pellets. After allowing the mixture to homogenize, the remaining portion of the impregnation solution was added slowly to the rotating extrudate. Following addition of the impregnation solution, the impregnated pellets were tumbled in the rotating impregnation vessel for approximately 10 minutes. The resultant wet impregnated Al₂O₃-dolomite TL pellets were air dry overnight followed by drying in a 40 L/hr flow of dry air at 120 °C for 12 hrs and calcined using heating rate of 2 °C/min to 600 °C and by holding at 600 °C for 6 hrs.

[0071] FIG. 8 is a plot of the percent methane conversion as a function of the time (hrs) on stream at a temperature of 425 °C for different guard bed materials placed in front of a MOC. Data were obtained by testing powder (315-500 µm fraction) guard bed/MOC samples in a 16 reactor high-throughput testing rig. For each guard bed/MOC run, a total of 2 mL of guard bed/MOC samples were loaded into each reactor of the test rig. A weight ratio of the guard bed powder to the MOC powder loaded in the respective reactors was maintained at approximately 1.9:1. The guard bed and MOC powders were

diluted with inert silicon carbide (SiC), 315-500 μ fraction, particles to achieve a volume of 1 mL for each respective guard bed and MOC powders. Table 2 below lists the guard bed formulations used for each respective run. The following operating conditions were used: GSHV = 100,000 h^{-1} , reactor temperature (RxT)= 425 °C. The exhaust gas feed composition was as follows: 2000 ppm CH_4 , 350 ppm CO, 4.5% CO_2 , 10.5% O_2 , 150 ppm NO, 12 percent volume (%vol) of H_2O , and N_2 for the remaining balance to 100%. The MOC used was a washcoated MOC catalyst having 4%wt Pd, 0.5%wt Pt, 0.125%wt Rh on ZrO_2 . The addition of 1.5 ppm of SO_2 to the exhaust gas feed was initiated at 25 hrs on stream and maintained for the duration of the tests.

Table 2. REACTOR RIG TEST GUARD BED RUNS 1-7 at 425 °C

RUN #	GUARD BED PREPARATION	GUARD BED COMPOSITION
1	---	No Guard Bed – Control
2	EXAMPLE 19	8%wt Mn/dolomite-derived guard bed
3	EXAMPLE 18	8% Al_2O_3 guard bed example 18
4	EXAMPLES 18 & 19	Physical mixture of 8%wt Mn/ Al_2O_3 +8%wt Mn/dolomite-derived guard bed
5	EXAMPLE 20 & 22	8%wt Mn/Peptized w/ Nitric Acid and Co-extruded pellets of Al_2O_3 and dolomite-derived particles
6	EXAMPLE 20 & 22	8%wt Mn/Peptized w/Nitric Acid and Co-extruded pellets of Al_2O_3 /dolomite-derived particles
7	EXAMPLE 21 & 22	8%wt Mn/Peptized w/Acetic Acid and Co-extruded pellets of Al_2O_3 /dolomite-derived particles

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[0072] As shown in FIG. 8, the data 142 indicates that, prior to the addition of SO_2 (1.5 ppm), all samples had approximately 92-97 % CH_4 conversion. Notably, the CH_4 conversion/oxidation activity was stable for all samples up until addition of the SO_2 . Following addition of the SO_2 at 25 hrs on stream, the CH_4 conversion/oxidation activity

of the MOC in the absence of the guard bed (Run 1) rapidly declined. For example, within 5 hrs after addition of the SO₂ the CH₄ conversion/oxidation activity of the MOC was less than 20% CH₄ conversion. In contrast, test runs having the disclosed guard bed, the MOC maintained a CH₄ conversion for a period of time longer than Run 1, which did not have the guard bed. For example, the CH₄ conversion of the MOC was improved when guard beds having the low porosity 8%wt Mn/dolomite-derived guard bed (Run 2) and the high porosity 8%wt Mn/Al₂O₃ guard bed sample (Run 3) were used. As shown by the data 142, the high porosity 8 %wt Mn/Al₂O₃ guard bed composition was better compared to the low porosity 8 %wt Mn/dolomite-derived guard bed formulation in improving the CH₄ conversion /methane oxidation activity of the MOC. Not wishing to be bound by theory, the improved CH₄ methane conversion/oxidation activity of the MOC may be attributed to the SO₂ conversion and capturing by active MnO₂ centers and Al₂O₃ or dolomite support surfaces of the disclosed guard bed formulations. Moreover, as illustrated in FIG. 8, MOC used in combination with the Al₂O₃ based guard bed had a better CH₄ conversion/oxidation activity compared to the dolomite-derived based guard bed. This may be due, in part, to a higher SO₂ uptake capacity of the higher pore volume (e.g., 0.868 mL/g) of the Al₂O₃ based guard bed compared to that of the lower pore volume (e.g., 0.17 mL/g) for the dolomite-derived based guard bed, For example, the higher porosity (e.g., pore volume) of the Al₂O₃ based guard bed provides for a greater MnO₂ dispersion and accessibility and, consequently, greater SO₂/SO₃ deposition and reactivity with and retention within the Al₂O₃ (in the form of Al₂(SO₄)₃) relative to the low porosity dolomite-derived based guard bed.

[0073] When using a physical mixture of the high porosity Al_2O_3 pellets and low porosity dolomite-derived pellets as in Run 4, the ability for the guard bed to capture SO_2 was improved and the CH_4 conversion /methane oxidation activity of the MOC was maintained for a longer period of time compared to runs using either the high porosity Al_2O_3 pellets (Run 3) and dolomite-derived pellets (Run 2) alone in the guard bed. However, in runs in which co-extruded high porosity Al_2O_3 and dolomite-derived pellets were used in the guard bed (e.g., Runs 5-7), the MOC unexpectedly exhibited significantly higher CH_4 conversion /methane oxidation stability compared to runs having discrete pellets of the Mn/ Al_2O_3 component (Run 3), the Mn/dolomite-derived component (Run 2), or a physical mixture of the Mn/ Al_2O_3 and Mn/dolomite-derived components (Run 4). For example, as shown by the data 142, the MOC used in combination with the guard beds having the co-extruded Al_2O_3 and dolomite-derived pellets (Runs 5-7) maintained CH_4 conversion/oxidation activity more than 40 hours after addition of the SO_2 . Not to be bound by theory, the unexpected CH_4 conversion/oxidation of the MOC when used in conjunction with the co-extruded Al_2O_3 /dolomite-derived pellets may be due, in part, to the fact that coextrusion of small Al_2O_3 and dolomite-derived particles and subsequent chemical bonding between them imparts the desired chemical functionality (both Al_2O_3 -and dolomite-derived active for catalytic poisons removing sites), a higher porosity (water pore volume of 0.50 to 0.55 mL/g for nitric acid and acetic acid, respectively) than dolomite particles alone, and accessibility into the relatively low porosity (water pore volume of 0.17 cc/g) dolomite-derived particles facilitate reactivity with SO_2 and other exhaust gas poisons molecules. It should be noted that in Run 7, the MOC used in conjunction with the guard bed having the 8%wt/ acetic acid peptized co-extruded Al_2O_3 and dolomite-derived particles) had

significantly better CH₄ conversion/oxidation activity stability relative to the nitric acid peptized analogs (Runs 5 and 6). This may be due, in part, to the greater pore forming ability of bulkier acetic acid molecule compared to nitric acid molecules.

[0074] In addition to testing the guard bed formulations disclosed herein at 425 °C, the guard bed formulations were tested for their ability to remove MOC poisons from the exhaust gas at higher temperatures (e.g., at 470 °C. FIG. 10 is a plot 146 of percent methane conversion as a function of time (hrs) on stream at 470 °C for different guard bed materials placed in front of an MOC. Similar to the samples discussed above with reference to FIG. 8, each reactor of the test rig was loaded with a total of 2 mL of guard bed/MOC. The guard bed powder to MOC powder loaded in each respective reactor had a weight ratio of approximately 1.9:1. Inert SiC was used to dilute the guard bed and MOC powders to yield a volume of 1 mL for each respective powder. Table 3 below lists the guard bed formulations used for each respective run. The operating conditions were as follows: GSHV = 100,000 h⁻¹ and RxT = 470 °C. The exhaust gas feed composition was as follows: 2000 ppm CH₄, 350 ppm CO, 4.5% CO₂, 10.5% O₂, 150 ppm NO, 12 percent volume (%vol) of H₂O and N₂ for the remaining balance. The MOC used was a washcoated MOC catalyst having 4%wt Pd, 0.5%wt Pt, 0.125%wt Rh on ZrO₂. The addition of 1.5 ppm of SO₂ to the exhaust gas feed was initiated at 25 hrs on stream and maintained for the duration of the tests.

Table 3. REACTOR RIG TEST GUARD BED RUNS 8-11 at 470 °C

RUN #	GUARD BED PREPARATION	GUARD BED COMPOSITION
8	---	No Guard Bed – Control
9	EXAMPLE 19	8%wt Mn/dolomite-derived guard bed

10	EXAMPLES 18 & 19	Physical mixture of 8%wt Mn/Al ₂ O ₃ +8%wt Mn/dolomite-derived guard bed
11	EXAMPLE 20 & 22	8%wt Mn/Peptized w/Nitric Acid and Co-extruded pellets of Al ₂ O ₃ and dolomite-derived particles

[0075] As shown in **FIG. 9**, data **148** indicates that, prior to the addition of SO₂, all samples resulted in approximately 99-100 % CH₄ conversion. However, upon the addition of SO₂ at 25 hrs on stream, the CH₄ conversion/oxidation activity of the control MOC sample without guard bed (Run 8) rapidly declined. In contrast, test runs having the disclosed guard bed components (Runs 9-11) positioned in front of the MOC bed enabled the MOC to maintain a desired CH₄ conversion/oxidation activity for greater than 10 hrs after addition of the SO₂. Similar to the data **142** in **FIG. 8**, the data **148** for samples having both the high porosity Al₂O₃ and the low porosity dolomite-derived powders resulted in improved CH₄ conversion/oxidation activity of the MOC. However, unexpectedly, at the higher operating temperature of 470 °C, the 8 %wt Mn on nitric acid peptized co-extruded Al₂O₃ and dolomite guard bed (Run 11) had significantly higher CH₄ conversion/oxidation activity relative to the control MOC sample and the other guard bed formulations. Accordingly, the performance data shown in FIGS. 5-9 clearly shows the substantial benefits and performance advantages of the guard beds formulations disclosed herein for efficient removal of SO₂ and other MOC poisons from exhaust gas generated by natural gas fueled engines.

[0076] Present techniques also include a method for methane emissions abatement in an exhaust gas generated in a natural gas operated engine system. **FIG. 10** is a flow diagram of an embodiment of a method **200** by which an exhaust gas emissions abatement system (e.g., the exhaust gas emissions abatement system **14** described above) may treat an exhaust

gas (e.g., the exhaust gas **28**) having methane and methane oxidation catalyst (MOC) poisons. The method **200** includes feeding (block **204**) an exhaust gas (e.g., the exhaust gas **28**) having CH₄ and catalyst poisons to an exhaust gas emissions abatement system (e.g., the exhaust gas emissions abatement system **14**) having a guard bed (e.g., the guard bed **36, 50, 96**), as described above with reference to **FIGS. 1-4**. The method **200** also includes passing (block **206**) the exhaust gas through a guard bed (e.g., the guard bed **36, 50, 96**). As discussed above, the guard bed may have a single layer or multiple layers of a MOC poisons capturing component. Additionally, the MOC poisons capturing component may be a single component or a multi-component material having a transition metal oxide supported on an Al₂O₃ support material, dolomite-derived support material, or both.

[0077] The method **200** also includes removing (block **208**) catalyst poisons from the exhaust gas to generate an intermediate exhaust gas (e.g., the intermediate exhaust gas **42**). For example, as discussed above, guard beds containing transition metal oxides and Al₂O₃ and dolomite-derived materials may react, convert, adsorb, and capture catalyst poisons making them unable to pass through the guard bed and adversely affect the performance and catalyst life of the MOC. The intermediate exhaust gas exiting the guard bed is substantially devoid of catalyst poisons that may adversely affect the catalytic performance/activity and overall useful life of the MOC.

[0078] The method **200** further includes passing (block **210**) the intermediate exhaust gas through a bed of MOC (e.g., the MOC bed **40**) and oxidizing and abating (block **212**) methane in the intermediate exhaust gas to generate a treated exhaust gas (e.g., the treated exhaust gas **50**) having less than approximately 150-200 ppmv of methane. By removing the catalyst poisons upstream of the MOC bed, the guard bed of the present disclosure

allows the MOC to fully exert its methane oxidation activity. That is, the MOC may efficiently and effectively convert more than approximately 80% of the methane in the intermediate exhaust gas. As such, the guard bed/MOC system disclosed herein provides for the treated exhaust gas released from the system to have methane emissions levels that

5 are at or below the desired or regulated emissions levels.

[0079] As described above, certain embodiments of the system and method disclosed herein may include a catalyst poisons capturing guard bed positioned upstream of a methane oxidation catalyst (MOC) bed. The guard bed includes one or more components that react, convert, adsorb, and thereby remove and/or capture catalyst poisons such as

10 sulfur dioxide (SO₂), phosphorus (P), zinc (Zn), calcium (Ca), silicon (Si) among others, that would otherwise poison and adversely affect the performance of the MOC in the methane abatement unit. The guard bed may include single or multiple layers having single MOC poisons capturing component or multiple MOC poisons capturing components arranged in a consecutive or mixed configuration. The MOC poisons capturing

15 components in the guard bed may include transition metals (in oxide form), aluminum oxide (Al₂O₃), dolomite-derived materials, or both. By employing the exhaust gas emissions abatement system of the present disclosure the methane present in exhaust gasses generated in lean-burning natural gas engines may be removed via methane oxidation catalysts in an effective and efficient manner. Accordingly, exhaust gasses released from

20 natural gas engines equipped with the exhaust gas emissions abatement system having the methane abatement unit disclosed herein may have methane emissions levels that are at or below the desired or regulated emission levels.

[0080] The present disclosure may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the disclosure is, therefore, indicated by the appended claims rather than by the foregoing description. All
5 changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

1. A system for removing methane oxidation catalyst (MOC) poisons from an exhaust gas, comprising:

5 a methane abatement unit configured to receive the exhaust gas comprising methane (CH_4) and the MOC poisons, wherein the methane abatement unit comprises:

 a guard bed configured to remove the MOC poisons from the exhaust gas and to generate an intermediate exhaust gas comprising the CH_4 and devoid of the MOC poisons, wherein the guard bed comprises a MOC poisons capturing component comprising a first transition metal
10 oxide, an aluminum oxide (Al_2O_3) support material, and a dolomite-derived support material; and

 a MOC bed fluidly coupled to and positioned downstream from the guard bed, wherein the MOC bed comprises a MOC and is configured to remove CH_4 from the intermediate exhaust gas to generate a treated exhaust gas having less than 200 parts per million volume (ppmv) CH_4 .

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2. The system of claim 1, wherein the MOC poisons capturing component is a physical mixture of a first component comprising the first transition metal oxide and the Al_2O_3 support material and a second component comprising a second transition metal oxide and the dolomite-derived support material, wherein the second transition metal oxide is the same or different from the first transition
20 metal oxide.

3. The system of claim 2, wherein a ratio of the first component and the second component in the physical mixture is between 2:1 and 1:2

4. The system of claim 1, wherein the MOC poisons capturing component is a co-extrudate of the first transition metal oxide, the Al_2O_3 support material, and the dolomite-derived support material such that the MOC poisons capturing component is a single component.

5

5. The system of claim 1, wherein the guard bed is a single layer bed.

6. The system of claim 1, wherein the guard bed is a multi-layer bed having a first layer comprising the first transition metal oxide and the Al_2O_3 support material and a second layer comprising a second transition metal oxide and the dolomite-derived support material, wherein the second transition metal oxide is the same or different from the first transition metal oxide.

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7. The system of claim 1, wherein the first transition metal oxide concentration in the MOC poisons capturing component is between 3-20% wt.

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8. The system of claim 1, wherein the dolomite-derived support material is dolomite ($\text{CaMg}(\text{CO}_3)_2$), calcium magnesium oxide (CaMgO_2), a mixture of lime (CaO) and MgO , or a combination thereof.

20

9. The system of claim 1, wherein the first transition metal oxide is an oxide of manganese (Mn), vanadium (V), copper (Cu), and combinations thereof.

10. A method for removing methane oxidation catalyst (MOC) poisons from an exhaust gas, comprising:

feeding the exhaust gas comprising methane (CH_4) and the MOC poisons to a methane abatement unit comprising a guard bed and a MOC bed fluidly coupled to and downstream from the guard bed;

contacting the exhaust gas with a MOC poisons capturing component disposed within the guard bed, wherein the MOC poisons capturing component comprises a first transition metal oxide, an aluminum oxide (Al_2O_3) support material, and a dolomite-derived support material; and

removing the MOC poisons from the exhaust gas to generate an intermediate exhaust gas devoid of MOC poisons and comprising the CH_4 .

11. The method of claim 10, wherein the step of contacting the exhaust gas with the MOC poisons capturing component comprises passing the exhaust gas through a single layer of the MOC poisons capturing component, wherein the MOC poisons capturing component is a co-extrudate of the first transition metal oxide, the Al_2O_3 support material, and the dolomite-derived support material.

12. The method of claim 10, wherein the step of contacting the exhaust gas with the MOC poisons capturing component comprises passing the exhaust gas through a single layer of the MOC poisons capturing component, wherein the MOC poisons capturing component is a physical mixture of a first component comprising the first transition metal oxide and the Al_2O_3 support material and a second component comprising a second transition metal oxide and the dolomite-derived support material, and wherein the second transition metal oxide is the same or different from the first transition metal oxide.

13. The method of claim 10, wherein the step of contacting the exhaust gas with the MOC poisons capturing component comprises passing the exhaust gas through a first MOC capturing component layer configured to remove a first portion of the MOC poisons and to generate an intermediate gas stream, and passing the intermediate gas steam through a second MOC poisons capturing component layer configured to remove a second portion of the MOC poisons and to generate the intermediate exhaust gas, wherein the first MOC capturing component layer comprises a first component having the first transition metal oxide and the Al_2O_3 support material and the second MOC poisons capturing layer comprises a second component having a second transition metal oxide and the dolomite-derived support material, and wherein the second transition metal oxide is the same or different from the first transition metal oxide.

14. The method of claim 10, comprising feeding the intermediate exhaust gas to the MOC bed having a MOC and removing the CH_4 from the intermediate gas to generate a treated exhaust gas having less than 200 parts per million volume (ppmv) CH_4 .

15. A methane oxidation catalyst (MOC) poisons capturing component for removing MOC poisons from an exhaust gas, comprising:

- an aluminum oxide (Al_2O_3) support material having a first porosity;
- a dolomite-derived support material having a second porosity that is less than the first porosity;
- a first transition metal oxide supported on the Al_2O_3 support material, the dolomite-derived support material, or both, wherein a concentration of the first transition metal oxide is between 1-25 weight % (wt %); and

wherein the MOC poisons capturing component removes sulfur dioxide (SO₂), phosphorus (P), calcium (Ca), zinc (Zn), silicon (Si) and ash.

16. The MOC poisons capturing component of claim 15, wherein the MOC poisons capturing component is a physical mixture of a first component comprising the first transition metal oxide and the Al₂O₃ support material and a second component comprising a second transition metal oxide and the dolomite-derived support material, wherein the second transition metal oxide is the same or different from the first transition metal.

17. The MOC poisons capturing component of claim 16, wherein a ratio of the first component and the second component in the physical mixture is between 2:1 and 1:2

18. The MOC poisons capturing component of claim 15, wherein the MOC poisons capturing component is a co-extrudate of the first transition metal oxide, the Al₂O₃ support material, and the dolomite-derived support material such that the MOC poisons capturing component is a single component

19. The MOC poisons capturing component of claim 15, wherein the dolomite-derived support material is dolomite (CaMg(CO₃)₂), calcium magnesium oxide (CaMgO₂), a mixture of lime (CaO) and MgO, or a combination thereof.

20. The MOC poisons capturing component of claim 15, wherein the transition metal oxide is an oxide of manganese (Mn), vanadium (V), copper (Cu), and combinations thereof.

21. The MOC poisons capturing component of claim 15, wherein the first porosity is greater than 2.0 milliliters (mL)/gram (g).

5 22. The MOC poisons capturing component of claim 15, wherein the second porosity is less than 0.2 mL/g.