REMOVAL OF CATALYST POISONS FROM GAS STREAMS

Field of the Invention

[1] The present disclosure relates generally to the field of removing catalyst poisons, including one or more sulfur species, from gas streams to generate reduced-poisons gas streams, where the catalyst poisons are detrimental to downstream catalysts used to treat the reduced-poisons gas streams.

Background of the Invention

[2] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present invention. This discussion is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the present invention. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of any prior art.

[3] For catalytic chemical reactions involving gas streams, it is generally desirable to have gas streams with minimal amounts of components that may undesirably impact catalyst performance and activity. Typical examples of undesirable components that may poison catalysts include various sulfur species such as sulfur dioxide (SO_2), sulfur trioxide (SO_3), hydrogen sulfide (H_2S), mercaptans, phosphorus, zinc, and/or calcium. These undesirable components are generally found in gas streams generated from hydrocarbon refining and combustion processes. Therefore, industries that can benefit from removing these catalyst poisons, particularly sulfur-containing catalyst poisons, in a gas stream prior to contacting it with a downstream catalyst include municipal waste incineration, O_2 removal for renewable natural gas (RNG) and natural gas conditioning, engine exhaust emissions control, caprolactam production process, and refinery fuel gas (RFG) fired furnace, heaters, and turbines among others. General methods of removing undesirable components from gas streams are known, particularly gas streams that come in contact with methane oxidation catalysts, which are known to be extremely sensitive to sulfur-containing species. For instance, WO2021262219 discloses systems and methods for removing methane oxidation catalyst (MOC) poisons from an exhaust gas using a methane abatement unit that includes a guard bed that may remove the MOC poisons from the exhaust gas. The guard bed includes a MOC poisons capturing component having a metal oxide from the first transition metal series, an aluminium oxide (Al_2O_3) support material, and a dolomite-derived support material. A drawback to the disclosed MOC poisons capturing component in WO2021262219 is the relatively

large amount of this component that may be required to protect the downstream MOC from poisoning such that the MOC's performance and activity remain at a desired level. That is, for the performance and activity of the MOC to not be negatively impacted and its lifespan improved, the required amount of the MOC poisons capturing component disclosed in WO2021262219 would be cost prohibitive. Therefore, in existing applications the amount of the MOC poisons capturing component in the guard bed is not sufficient to fully protect the MOC. Consequently, the MOC, which is extremely sensitive to sulfur, has a shortened lifespan and is frequently replaced, thereby increasing the overall operational costs of methane abatement processes. The same holds true for other sulfur-sensitive catalysts (e.g., vanadium titania catalyst and noble metal catalyst, among others). It is well known in the art that certain transition and noble metals catalysts are sensitive to sulfur. Accordingly, there is a current need to provide poison capturing components that more effectively and efficiently remove catalyst poisons, particularly sulfur species, from a gas stream before coming in contact with certain catalysts compared to existing poison capturing components such that catalyst lifespan is improved and the overall operational cost of catalytic processes is reduced.

Summary of the Invention

[4] It is widely known that hopcalite catalysts (e.g., copper (Cu) manganese (Mn) catalysts) are effective for converting carbon monoxide to carbon dioxide. For example, hopcalite catalysts have been known and used since at least 1920 (see, for example, US1345323) to oxidise carbon monoxide to form carbon dioxide. It is also known that hopcalite catalysts can be used to remove hydrogen from gas streams, which can be found in EP4088807. Similarly, US6511640 discloses the use of hopcalite catalysts (e.g., CARULITE®-300) to remove carbon monoxide and hydrogen from air. EP2662653 and EP2789376 both disclose the removal of both hydrogen and carbon monoxide impurities from a dry gas at low temperature (0°C to 60°C) using only hopcalite catalyst. It has now been discovered that these catalysts can also be used as an adsorbent to remove catalyst poisons, including but not limited to one or more sulfur-containing species, such as sulfur dioxide (SO_2), sulfur trioxide (SO_3), and/or hydrogen sulfide (H_2S). For purposes of this specification, the terms "adsorption" and "absorption" (and their grammatical equivalents) have the same, all-inclusive meaning. Embodiments of methods and systems disclosed herein can prolong the life and/or performance of one or more catalysts (such as a methane oxidation catalyst – MOC, NOx reduction catalysts, and other transition and/or noble metal catalysts) that are sensitive to catalytic

poisons (such as one or more sulfur-containing species) by removing at least one sulfur-containing species from a gas stream prior to providing the gas stream to the catalyst. The present disclosure provides MOC as an example of a suitable downstream catalyst which may have its performance prolonged by placing a hopcalite component for poison removal upstream of it. It is understood that while the context of the present disclosure is discussed in terms of the MOC, it is not intended to limit the scope of the disclosure, which can be applied to any suitable downstream catalyst, such as those sensitive to sulfur-poisoning. By way of non-limiting example, such sulfur sensitive catalysts include those transition and/or noble metal catalysts used to reduce emissions of harmful compounds into the atmosphere, to remove from a gas stream one or more of the following compounds: nitrogen oxides (NOx), volatile organic compounds (VOC), methane, carbon monoxide (CO), nitrous oxide (N_2O), dioxins, and ammonia (NH_3), or any other sulfur sensitive catalyst. Using a hopcalite component as an adsorbent to remove one or more sulfur species can also benefit catalysts that remove oxygen (O_2) for renewable natural gas or natural gas conditioning. By way of non-limiting example, industries that can benefit from the embodiments disclosed herein include municipal waste incineration, engine exhaust emissions control, caprolactam production process, and/or refinery fuel gas (RFG), fired furnace, heaters, and turbines.

[5] In addition, it has further been discovered that hopcalite has a higher sulfur storage capacity as compared to the MOC poisons capturing component disclosed in WO2021262219, which allows hopcalite to be used as a sulfur-removal catalyst. It has still further been discovered that as the total pore volume of hopcalite increases, removal of sulfur-species from a gas stream also increases, thereby improving the lifespan and/or performance of a downstream sulfur-sensitive catalyst such as, for example, MOC. Therefore, an operator may select the hopcalite based on its total pore volume depending on the sulfur sensitivity of the catalyst positioned downstream from it. Unlike the poison capturing component disclosed in WO2021262219, the hopcalites disclosed herein are relatively cost effective catalysts that can enable the design and construction of compact and lower cost guard beds to remove sulfur species from a gas stream prior to it being treated with a sulfur sensitive downstream catalyst.

[6] According to one aspect, there is provided a method for improving lifespan of a methane oxidation catalyst employed in a methane reduction step. The method comprises providing a feed gas stream comprising methane (CH_4), preferably in an amount in a range from

100 ppm and up to 10000 ppm, and optionally carbon dioxide and oxygen, and at least one sulfur-containing compound to a methane abatement unit comprising a guard bed upstream of a methane oxidation bed, where the guard bed comprises a compound to capture an amount of the at least one sulfur-containing compound and wherein the methane oxidation bed comprises a methane oxidation catalyst to remove an amount of methane from the feed gas stream. The method further comprises providing the guard bed with hopcalite to capture an amount of the at least one sulfur-containing compound.

[7] Optionally, the feed gas stream is provided to the methane abatement unit at a temperature in a range from 300 °C and up to 600 °C, preferably from 390 °C and up to 580 °C.

[8] Optionally, the hopcalite comprises at least one, including all, of the following: (i) a molar ratio of manganese to copper in a range from 1.5:1 and 7:1, preferably from 2:1 and up to 5:1, more preferably from 2.25:1 and up to 4:1, most preferably 2.5:1 and up to 3:1; (ii) a surface area (N_2 BET) of greater than 70 m^2/g, preferably greater than 140 m^2/g, more preferably greater than 180 m^2/g, and most preferably greater than 200 m^2/g; (iii) and a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g. Optionally, the hopcalite comprises a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g.

[9] Optionally, the hopcalite comprises MnO_2 in an amount in a range from 60 mol% and up to 90 mol%; CuO in an amount in a range from 10 mol% and up to 40 mol%, Al_2O_3 in an amount of less than 10 mol%; CaO in an amount of less than 2 mol%; and K_2O in an amount of less than 2 mol%.

[10] Optionally, the hopcalite provides greater than 10% sulfur storage under test conditions: Gas Hourly Space Velocity (GHSV): 210 L/g-hr; Temperature: 425°C; and Feed Composition: 670 ppm CH_4, 120 ppm CO, 4.5% CO_2, 11.5% O_2, 150 ppm NO, 10.5% H_2O, and 1.5ppm SO_2.

[11] Optionally, the hopcalite is capable of maintaining methane conversion activity of the MOC of at least 50% for at least 200 hours under test conditions: Gas Hourly Space Velocity (GHSV): 210 L/g-hr; Temperature: 425°C; Feed Composition: 670 ppm CH_4, 120 ppm CO, 4.5% CO_2, 11.5% O_2, 150 ppm NO, 10.5% H_2O, and 1.5ppm SO_2.

[12] Optionally, the gas stream consists essentially of exhaust feed gas.

[13] Optionally, the sulfur species is selected from the group consisting of sulfur dioxide (SO_2), sulfur trioxide (SO_3), and any combination thereof.

[14] According to another aspect, there is provided a system for removing methane oxidation catalyst (MOC) poisons from a feed gas. The system comprises a guard bed configured receive a feed stream comprising methane (CH_4) in an amount in a range from 100 ppm and up to 5000 ppm, and optionally carbon dioxide and oxygen, and at least one sulfur species, wherein the guard bed comprises a hopcalite to remove an amount of the at least one sulfur species to provide a reduced-sulfur feed stream; and a MOC bed configured to receive the reduced-sulfur feed stream and contact it with a MOC to remove an amount of CH_4 to provide a treated feed stream.

[15] Optionally, the hopcalite comprises at least one, including all, of the following: (i) a molar ratio of manganese to copper in a range from 1.5:1 and 7:1, preferably from 2:1 and up to 5:1, more preferably from 2.25:1 and up to 4:1, most preferably 2.5:1 and up to 3:1; (ii) a surface area (N_2 BET) of greater than 70 m^2/g, preferably greater than 140 m^2/g, more preferably 180m2/g, and most preferably 200m2/g; (iii) and a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g. Optionally, the hopcalite comprises a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g.

[16] Additional features and advantages of exemplary implementations of the disclosure 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 appended claims or may be learned by the practice of such exemplary implementations as set forth hereinafter.

Brief Description of the Drawings

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

[18] FIG. 1 is a block diagram of a methane abatement unit comprising an upstream guard bed in accordance with an embodiment of the present disclosure;

[19] FIG. 2 is a comparative plot of percent methane conversion as a function of time on stream for a methane oxidation catalyst (MOC) positioned downstream from guard beds having a hopcalite compared to no guard bed, whereby the hopcalite in each respective guard bed has a different total pore volume; and

[20] FIG. 3 is comparative plot of percent methane conversion as a function of time on stream for the MOC positioned downstream from a guard bed having hopcalite B as compared to no hopcalite and a reference catalyst.

Detailed Description of the Invention

[21] The present invention will now be described in detail with reference to embodiments thereof as illustrated in the accompanying drawings. References to "one embodiment," "an embodiment," "an example embodiment," etc., indicate that the embodiment described may include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which would be apparent to those skilled in the art, are within the spirit and scope of the invention.

[22] Although the description herein provides numerous specific details that are set forth for a thorough understanding of illustrative embodiments, it will be apparent to one skilled in the art that embodiments may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not unnecessarily obscure the present invention. The features and advantages of embodiments may be better understood with reference to the drawings and discussions that follow.

[23] In addition, when like elements are used in one or more figures, identical reference characters will be used in each figure, and a detailed description of the element will be provided only at its first occurrence. Some features or components of the systems or processes described herein may be omitted in certain depicted configurations in the interest of clarity.

[24] There are many processes that may benefit from placement of a guard bed (e.g., a sulfur guard bed) upstream of a catalyst. In particular, processes using catalysts that are sensitive to

certain contaminants (e.g., sulfur) in a feed stream that impact catalyst performance and activity. These processes include, but are not limited to, those that use catalysts for the removal of nitrogen oxides (NOx), volatile organic compounds (VOC), methane (CH_4), carbon monoxide (CO), nitrous oxide (N_2O), dioxins, and ammonia (NH_3) from a gas stream. To facilitate discussion, the present disclosure will be described in the context of a process for methane abatement of an exhaust feed stream from a combustion engine, particularly one that runs on natural gas. However, it is understood that the embodiments described herein may be used in other processes such as, for example, municipal waste incineration, O_2 removal for renewable natural gas (RNG) and natural gas conditioning, engine exhaust emissions control, caprolactam production process, and refinery fuel gas (RFG) fired processes that use furnace, heaters, and/or turbines without departing from the scope of the invention. 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, diesel, coal, etc.) for engines in stationary (power, drilling etc.) and transport (marine, railroad, and other on road) applications. Under certain operating conditions, the combustion of natural gas may not be complete. 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 CH_4. It is desirable to develop and deploy an exhaust gas emissions abatement system that may remove or decrease the amount of CH_4 in the feed gas, in light of the potential greenhouse effect of CH_4.

[25] One technique for CH_4 abatement includes oxidation of CH_4 in the presence of a methane oxidation catalyst (MOC). In methane oxidation techniques, hot CH_4-containing exhaust gas contacts the MOC, which in the presence of O_2 catalytically converts CH_4 into CO_2 and H_2O. Generally, MOCs used for CH_4 abatement include at least one active metal oxide supported on a porous inorganic oxide support. A suitable example may include noble metal oxides, such as platinum (Pt), palladium (Pd), silver (Ag), iridium (Ir), 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.). Noble metal, however, are sensitive to chemical species such as SO_2, P, Zn, Ca, and Si that are generally present in the exhaust gas. For instance, in addition to any unburned CH_4, the combustion gas from the natural gas engine also typically contains small levels (between approximately 0.1 to approximately 8 parts per

million (ppm)) of sulfur dioxide (SO_2), which comes from small levels 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. In addition to any unburned CH_4 and SO_2, the combustion gas from natural gas engines can also contain 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.

[26] SO_2, P, Zn, Ca, and Si, among others, are referred to as MOC poisons. As such, the performance and life of the MOC for CH_4 oxidation are adversely affected by some of these chemical species, particularly SO_2. Therefore, it is desirable to develop and deploy, in conjunction with natural gas engines, equipment to capture one or more sulfur-containing species from the exhaust gas to prolong the life and maintain the performance of the MOC.

[27] It has been found that hopcalites have a relatively high sulfur storage capacity (at least 10% under certain conditions as described further below), which is beneficial for use in a sulfur guard bed positioned upstream of a sulfur-sensitive catalyst (e.g., MOC) that is used to remove undesirable components (e.g., CH_4) from a gas stream, such as an exhaust gas stream, to prolong the lifespan of the catalyst.

[28] Turning to FIG. 1, the present disclosure provides a method for improving the lifespan of, for example, a methane oxidation catalyst employed in a methane reduction step. The method includes providing a feed gas stream 102 having methane (CH_4) to a methane abatement unit 100. The methane abatement unit 100 includes a guard bed 104 upstream of a methane oxidation bed 106. The guard bed 104 has a catalyst (not shown) to capture an amount of at least one sulfur-containing compound from the feed gas stream 102, and the methane oxidation bed 106 includes a methane oxidation catalyst (not shown) to remove an amount of methane from the feed gas stream 102.

[29] The method further includes providing the guard bed 102 with hopcalite as the catalyst to capture an amount of at least one sulfur-containing compound from the feed gas stream 102. The feed gas stream 102 is provided to the methane abatement unit 100 at a flow rate and operating pressure that can vary, depending on the application and as known to one of ordinary skill. For instance, the temperature range of the gas stream is from 300 °C and up to 650 °C, preferably from 390 °C and up to 580 °C.

[30] Any hopcalite or combination of hopcalites as known to one of ordinary skill may be suitable for use to capture an amount of at least one sulfur-containing compound in the guard bed

104. As used herein, the term "hopcalite" and its variants such as "hopcalite component" and "hopcalite catalyst," have their ordinary meaning as known to one of ordinary skill, including being generic terms for a range of catalysts typically comprising primarily (such as at least 50 wt%) a mixture of manganese oxide and copper oxide (see, e.g., US1345323), which can be prepared via various suitable methods such as precipitation, impregnation, sol-gel, reactive grinding, pyrolysis, physical mixing, and any combination thereof. For instance, a suitable hopcalite for use according to aspects of this present disclosure generally has at least one of the following: (i) a molar ratio of manganese to copper in a range from 1.5:1 and 7:1, preferably from 2:1 and up to 5:1, more preferably from 2.25:1 and up to 4:1, most preferably 2.5:1 and up to 3:1; (ii) a surface area (N_2 BET) of greater than 70 m^2/g, preferably greater than 140 m^2/g, more preferably greater than 180 m^2/g, and most preferably greater than 200 m^2/g; (iii) and a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g. Optionally, the hopcalite provided to the guard bed 104 includes MnO_2 in an amount in a range from 60 mol% and up to 90 mol%; CuO in an amount in a range from 10 mol% and up to 40 mol%, Al_2O_3 in an amount of less than 10 mol%; CaO in an amount of less than 2 mol%; and K_2O in an amount of less than 2 mol%. In a preferred embodiment, the MnO_2 is 75 mol% and the CuO is 25 mol%. However, in certain embodiments, such as those that have NO_x reduction catalysts or other less sensitive sulfur catalysts compared to MOC, the hopcalite may have less than 60 mol% MnO_2. For example, in these embodiments, the hopcalite may have between 40 and 50 mol% MnO_2.

[31] The surface area of the hopcalite, measured as N_2 BET, can be determined by suitable methods known to one of ordinary skill. An example of such methods includes the Brunauer-Emmett-Teller (BET) surface area analysis (ASTM test method D3663), which is a multi-point measurement of an analyte's specific surface area (m^2/g) through gas adsorption analysis, where an inert gas such as nitrogen is continuously flowed over a solid sample. The total pore volume of the hopcalite, as measured in cc/g, can be determined by suitable methods known to one of ordinary skill. An example of such methods includes Mercury intrusion porosimetry (MIP), ASTM test method D4284, which is a pore size measurement technique that uses non-wetting liquid penetration to measure the size and volume of pores in a wide range of porous solids.

[32] As noted, it has been discovered that hopcalite provides greater than 10% sulfur storage, preferably greater than 15%, under the test conditions listed in Table 1 below. Additional

details are provided in the Experiments portion. The sulfur storage can be determined by means known to one of ordinary skill. For instance, after the hopcalite has been exposed to sulfur under the conditions set forth in Table 1, such as at the end of the test, a portion of the respective hopcalite exposed to sulfur was tested for the amount of sulfur with respect to its mass using a LECO CS844 or CS230 instrument, or the like, to measure carbon and sulfur deposit on the hopcalite. As discussed in further detail below and illustrated in Table 2, the sulfur storage amount by the hopcalite is significantly greater than (about at least 3x) the sulfur storage amount of the MOC catalyst poison capturing component disclosed by WO2021262219A1. Based on the results of Experiment 1, the hopcalite disclosed herein may be used in guard beds that capture sulfur in a gas stream in processes where the sulfur amount in the gas stream is 2 ppm or less. Such processes include those having a sulfur guard bed upstream of an MOC bed, or any other bed that contains a catalyst that is sensitive to sulfur-poisoning. The sulfur in the feed gas stream can be in one or more sulfur-containing species, such as sulfur dioxide (SO_2), sulfur trioxide (SO_3), and any combination thereof.

Table 1. Test conditions

Condition	Amount
Gas Hourly Space Velocity (GHSV)	210 L/g-hr
Powder testing	315 – 500 micron
Temperature	425°C
Feed Composition	• 670 ppm CH_4 • 120 ppm CO • 4.5% CO_2 • 11.5% O_2 • 150 ppm NO • 10.5% H_2O • 1.5ppm SO_2

[33] In addition, it has been further discovered that as the total pore volume of the hopcalite increases, the amount of sulfur removed from the gas stream also increases, indicating that hopcalites having a higher pore volume tend to remove/capture more sulfur compared to hopcalites having a lower pore volume, thereby better protecting the sulfur sensitive downstream catalyst

from poisoning and increasing its lifespan. For example, FIG. 2 illustrates a plot of % CH_4 conversion with respect to time on stream for MOC positioned downstream from guard beds that each contain a hopcalite having a respective total pore volume. As shown in FIG. 2, the hopcalite having a total pore volume of 0.4 cc/g (INV. EXP. 3) had the lowest sulfur storage capacity compared to those having larger total pore volumes (INV. EXP. 1, 2, and 4), as demonstrated by the level of CH_4 conversion over time of the MOC. As the total pore volume of the hopcalite used in the guard bed increases, more poisonous sulfur is removed from the gas stream and the MOC is able to maintain CH_4 conversion above 80% for longer periods of time. Table 2 below illustrates that over 17% sulfur was adsorbed into the hopcalite having 0.7 cc/g total pore volume compared to 14% sulfur absorbed into the hopcalite having 0.4 cc/g total pore volume. For MOCs, which are extremely sensitive to sulfur poisoning, the 3% difference in sulfur removal between INV. EXP. 1 and 2 is significant. However, catalysts that are not as sensitive to sulfur poisoning compared to MOC, may benefit from a guard bed having a hopcalite with a total pore volume of at least 0.4 cc/g. As such, in accordance with an embodiment of the present disclosure, the method as described herein can further include providing the guard bed 104 with a hopcalite having a pore volume capable of maintaining the CH_4 conversion activity of the MOC at a level of at least 50%, preferably 65%, more preferably at least 80%, for at least 200 hours under the test conditions set forth in Table 1. For example, a hopcalite that is capable of maintaining a relatively high level of methane conversion activity for at least 200 hours as noted has a total pore volume of at least 0.5 cc/g, preferably at least 0.7 cc/g, and a sulfur storage capacity of at least 15%.

Examples

[34] Set forth below are experiments illustrating the performance of the hopcalite, as disclosed herein, when used in a guard bed upstream of a sulfur sensitive catalyst (e.g., MOC). Each of the experiments below were generally run using hopcalites with different total pore volumes. For reference, performance tests were conducted without any upstream adsorbent (COMPARATIVE EXAMPLE 1), and with the guard bed adsorbent or compound disclosed in WO2021262219 (hereinafter referred to as the "reference adsorbent") in another experiment (COMPARATIVE EXAMPLE 2). Also, as reference, the sulfur storage capacity was tested for the different hopcalites, each with a different total pore volume, and the reference adsorbent (Table 2). In experiments demonstrating the capability of a hopcalite to maintain CH_4 conversion activity of the MOC (INVENTIVE EXAMPLES 1-4), the MOC formulation used throughout the

experiments was as follows: (Pd (4 %wt) Pt (0.5 %wt) on a zirconium (ZrO_2) support. The powder (315-500 μm fraction) guard beds with the different hopcalites were prepared using any suitable technique known in the art.

[35] The experiments were run in a high throughput powder catalyst testing unit under the following conditions. A total of 2 mL of the guard bed and MOC samples were loaded into each reactor of the test unit in the following manner. The weight ratio of the various respective guard beds versus the MOC powders loaded in the reactors was maintained at approximately 1.9:1 (0.400g:0.213g). Once the guard bed and MOC powder amounts were measured, they were diluted with inert SiC (315-500 μ fraction) particles to achieve the volume of 1 mL of each: guard bed and MOC for a total of 2 mL. The data for each experiment was obtained under the conditions set forth in Table 1. The feed composition mimics a typical exhaust gas composition mimicking feed stream with the following gas composition: 670 ppm CH_4, 120 ppm CO, 4.5% CO_2, 10.5% O_2, 150 ppm NO, 10.5 (%vol) of H_2O and N_2 for the remaining balance to 100%. After allowing the temperature to stabilize at 425 °C, the injection of 1.5 ppm of SO_2 to the feed was initiated and maintained for the duration of the experiments ("Time on Stream" or "TOS"). The point of injection is reflected as 0 hr in FIGS. 2 and 3. The duration of the experiments for INVENTIVE EXAMPLES 1-4 was the same.

[36] The reference guard bed adsorbent (COMPARATIVE EXAMPLE 2) has a composition of 8 wt% Mn that is peptized with nitric acid and co-extruded with pellets of Al_2O_3 and dolomite-derived particles. Hopcalite A (INVENTIVE EXAMPLE 1) has a composition of 44 wt% Mn and 22 wt%: Cu and a total pore volume of about 0.4 cc/g. Hopcalite B (INVENTIVE EXAMPLE 2) has a composition of 41 wt% Mn and 16 wt% Cu and a total pore volume of about 0.8 cc/g. Hopcalite C (INVENTIVE EXAMPLE 3) has a composition of 41 wt% Mn and 16 wt% Cu and a total pore volume of about 0.7 cc/g. Hopcalite D (INVENTIVE EXAMPLE 4) 41 wt% Mn and 16 wt% Cu and a total pore volume of about 0.55 cc/g.

[37] As discussed above, FIG. 2 illustrates the performance of the MOC (% methane conversion) with respect to time on stream (TOS) after sulfur injection without the presence of a guard bed catalyst upstream of the MOC (COMPARATIVE EXAMPLE 1) and with the presence of a guard bed having hopcalites A-D positioned upstream of the MOC (INVENTIVE EXAMPLES 1-4, respectively) in accordance with embodiments of the present disclosure. As can be seen, hopcalite A increased the life of the MOC by 70%.

[38] FIG. 3 is a plot illustrating the performance of the MOC (% methane conversion) with respect to TOS after the sulfur injection in the absence of an upstream adsorbent (COMPARATIVE EXAMPLE 1), with the presence of a guard bed having the reference adsorbent positioned upstream of the MOC (COMPARATIVE EXAMPLE 2) and with the presence of a guard bed having the hopcalite B positioned upstream of the MOC (INVENTIVE EXAMPLE 2). As can be seen, the presence of a guard bed having the reference adsorbent prolonged the methane conversion performance of the MOC by 2.3 times, as disclosed by WO2021262219, compared to no guard bed (i.e., no adsorbent). However, a decline in methane conversion activity when using the reference adsorbent in the guard bed begins after about 41 hours and reaches the methane conversion level of having no guard bed within 50 hours on stream. Surprisingly, when the hopcalite B was used as the guard bed adsorbent, the methane conversion activity of the respective downstream MOC was prolonged significantly. Specifically, the methane conversion activity in INVENTIVE EXAMPLE 2 remained at 90% when the COMPARATIVE EXAMPLE 2 began to decline. Notably, the methane conversion activity of the hopcalite B disclosed herein remained at approximately 80% or higher for over 400 hours, almost 450 hours, before declining.

[39] As discussed above, the guard bed materials (e.g., the reference adsorbent and hopcalites A-D) were tested for sulfur storage capacity. For example, at the end of the MOC performance testing, the respective guard bed materials are sulfided. A portion of the sulfided guard bed materials were tested to determine the amount of sulfur with respect to its mass to provide the respective sulfur storage capacity, in wt%. Briefly, the sulfided guard bed materials were heated to a temperature in excess of 1500 °C via induction in pure oxygen causing the sulfur on these materials to be released into a gas. The resultant effluent gas is scrubbed for moisture, and optionally halogens, before being analyzed for sulfur dioxide via infrared spectroscopy. The sulfur content in the scrubbed gas was analyzed and used to determine the sulfur storage capacity of the respective guard bed material. As shown in Table 2, each hopcalite A-D have a significantly greater sulfur storage capacity compared to the reference adsorbent. For example, the hopcalites disclosed herein had a sulfur storage capacity of between approximately 14 and 17.5 wt% compared to less than 5 wt% for the reference adsorbent. Also, FIG. 2 shows that despite the hopcalite A (INVENTIVE EXAMPLE 1) picking up a significant amount of sulfur (e.g., 14.76 wt%), a decline of less than 80% CH_4 conversion of the MOC was observed after approximately 40 hours on stream indicating that the hopcalite A was not able to fully protect the MOC catalyst

from poisoning. In contrast, the activity of the MOC when the guard bed had the hopcalites B-D maintained 80% CH_4 conversion for greater than 300 hours on stream. This suggests that the higher the pore volume of the hopcalite, the higher the efficiency of sulfur removal from the gas stream. As noted above, hopcalite A resulted in a decline of MOC activity after 40 hours on stream. However, hopcalite A may be a suitable guard bed material for catalysts that are less sensitive to sulfur poisoning compared to MOC. For example, hopcalite A may be used as a guard bed material for catalysts such as NO_x reduction catalysts, which are less sensitive to sulfur compared to MOC.

[40] As discussed above, with reference to FIG. 2, using hopcalite B in a guard bed upstream of the MOC maintained the CH_4 conversion of the MOC at greater than 80% for more than 400 hours on stream compared to using hopcalite A in the guard bed, which resulted in less than 80% CH_4 after about 40 hours on stream. This is indicative of the superior sulfur removal capacity of the hopcalite B. While hopcalite A was still able to remove sulfur from the gas stream, its sulfur storage capacity is significantly less than that of hopcalite B. Therefore, the higher the total pore volume of the hopcalite (e.g., 0.8 cc/g compared to 0.4 cc/g) the more sulfur storage capacity and the more protected sulfur-sensitive catalyst are from sulfur poisoning.

Table 2. Sulfur Removal

	Total Pore Volume (cc/g)	%S
COMPARATIVE EXAMPLE 1 (No upstream adsorbent)	N/A	N/A
COMPARATIVE EXAMPLE 2 (Reference Adsorbent)	N/A	4.5
INVENTIVE EXAMPLE 1 (Hopcalite A)	0.4	14.76
INVENTIVE EXAMPLE 3 (Hopcalite B)	0.7	16.35
INVENTIVE EXAMPLE 2 (Hopcalite C)	0.8	17.15

INVENTIVE EXAMPLE 4 (Hopcalite D)	0.55	15.62

[41] The technical effects of the guard bed materials disclosed herein, specifically the hopcalites, are that these materials significantly improve the lifespan of sulfur sensitive catalysts by removing sulfur from gas streams prior to these gas streams coming in contact with the sulfur sensitive catalyst. It is believed that the Examples and Figures herein demonstrate that, surprisingly, hopcalites effectively and efficiently capture and remove sulfur from a gas stream. More surprisingly there is a relationship between the total pore volume of the hopcalite and the suflur storage capacity. As such, operators may select from a range of hopcalites with different pore volumes based on the sulfur sensitivity of the catalyst used downstream of it. For example, for applications of prolonging or improving the activity of a downstream catalyst, such as prolonging methane conversion activity of a downstream MOC, it may be desirable to select a hopcalite with greater total pore volume, for instance, at least 0.4 cc/g, for even greater improved protection of the catalyst, such as the MOC.

[42] While specific embodiments have been described herein, it is understood that such descriptions are not intended to limit the described embodiments. Instead, any combination of the features and elements provided above, whether related to different embodiments or not, is contemplated to implement and practice contemplated embodiments. Furthermore, although embodiments disclosed herein may achieve advantages over other possible solutions or over the prior art, whether or not a particular advantage is achieved by a given embodiment is not limiting of the scope of the present disclosure. Thus, the aspects, features, embodiments and advantages described herein are merely illustrative and are not considered elements or limitations of the appended claims except where explicitly recited in a claim(s).

CLAIMS

1. A method for improving lifespan of a methane oxidation catalyst employed in a methane reduction step, the method comprising:
    a. providing a feed gas stream (102) comprising methane (CH_4), preferably in an amount in a range from 100 ppm and up to 10000 ppm, and optionally carbon dioxide and oxygen, and at least one sulfur-containing compound to a methane abatement unit (100) comprising a guard bed (104) upstream of a methane oxidation bed (106), wherein the guard bed (104) comprises a compound to capture an amount of the at least one sulfur-containing compound and wherein the methane oxidation bed (106) comprises a methane oxidation catalyst to remove an amount of methane from the feed gas stream (102); and
    b. providing the guard bed (104) with hopcalite to capture an amount of the at least one sulfur-containing compound.

2. The method of claim 1 wherein the feed gas stream (102) being provided to the methane abatement unit (100) at a temperature in a range from 300 °C and up to 600 °C, preferably from 390 °C and up to 580 °C.

3. The method of any of the preceding claims, wherein the hopcalite comprises at least one, including all, of the following: (i) a molar ratio of manganese to copper in a range from 1.5:1 and 7:1, preferably from 2:1 and up to 5:1, more preferably from 2.25:1 and up to 4:1, most preferably 2.5:1 and up to 3:1; (ii) a surface area (N_2 BET) of greater than 70 m^2/g, preferably greater than 140 m^2/g, more preferably greater than 180 m^2/g, and most preferably greater than 200 m^2/g; (iii) and a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g.

4. The method of claim 3, wherein the hopcalite comprises a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g.

5. The method of any of the preceding claims, wherein the hopcalite comprises MnO_2 in an amount in a range from 60 mol% and up to 90 mol%; CuO in an amount in a range from 10 mol% and up to 40 mol%, Al_2O_3 in an amount of less than 10 mol%; CaO in an amount of less than 2 mol%; and K_2O in an amount of less than 2 mol%.

6. The method of any of the preceding claims, wherein the hopcalite provides greater than 10% sulfur storage under test conditions:
    a. Gas Hourly Space Velocity (GHSV): 210 L/g-hr
    b. Temperature: 425°C.
    c. Feed Composition: 670 ppm CH_4, 120 ppm CO, 4.5% CO_2, 11.5% O_2, 150 ppm NO, 10.5% H_2O, and 1.5ppm SO_2.

7. The method of any of the preceding claims, wherein the hopcalite being capable of maintaining methane conversion activity of the MOC of at least 50% for at least 200 hours under test conditions:
    a. Gas Hourly Space Velocity (GHSV): 210 L/g-hr
    b. Temperature: 425°C.
    c. Feed Composition: 670 ppm CH_4, 120 ppm CO, 4.5% CO_2, 11.5% O_2, 150 ppm NO, 10.5% H_2O, and 1.5ppm SO_2.

8. The method of any of the preceding claims, wherein the gas stream consists essentially of exhaust feed gas.

9. The method of any of the preceding claims, wherein the sulfur species is selected from the group consisting of sulfur dioxide (SO_2), sulfur trioxide (SO_3), and any combination thereof.

10. A system for removing methane oxidation catalyst (MOC) poisons from a feed gas, comprising:

- a guard bed configured receive a feed stream comprising methane (CH_4) in an amount in

a range from 100 ppm and up to 5000 ppm, and optionally carbon dioxide and oxygen, and at least one sulfur species, wherein the guard bed comprises a hopcalite to remove an amount of the at least one sulfur species to provide a reduced-sulfur feed stream; and

- a MOC bed configured to receive the reduced-sulfur feed stream and contact it with a MOC to remove an amount of CH_4 to provide a treated feed stream.

11. The system of claim 9, wherein the hopcalite comprises at least one, including all, of the following: (i) a molar ratio of manganese to copper in a range from 1.5:1 and 7:1, preferably from 2:1 and up to 5:1, more preferably from 2.25:1 and up to 4:1, most preferably 2.5:1 and up to 3:1; (ii) a surface area (N_2 BET) of greater than 70 m^2/g, preferably greater than 140 m^2/g, more preferably 180m2/g, and most preferably 200m2/g; (iii) and a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g.

12. The system of any one of claims 10 and 11, wherein the hopcalite comprises a total pore volume of greater than 0.4 cc/g, preferably greater than 0.6 cc/g, more preferably greater than 0.7 cc/g, and most preferably greater than 0.8 cc/g.