

PRETREATMENT DESULFURIZATION METHOD FOR SHIP FUEL OIL USING PRETREATMENT DESULFURIZATION AGENT

Technical Field

5 **[0001]** The present invention relates to a marine fuel oil pretreatment desulfurization method using a pretreatment desulfurization agent. More particularly, the present invention relates to a marine fuel oil pretreatment desulfurization method using a pretreatment desulfurization agent having a pretreatment desulfurization function, the method being capable of absorbing and reducing sulfur oxides (SO_x) when marine fuel oil such as bunker C oil commonly used as a fuel
10 for a marine engine is burned, thereby reducing sulfur oxides (SO_x) emissions during combustion of marine fuel oil.

Background Art

[0002] Sulfur oxides (SO_x) and nitrogen oxides (NO_x) are pointed out as pollutants that cause air
15 pollution. In particular, sulfur oxides are contained in industrial flue gas emitted during the combustion of fossil fuels containing sulfur, and the sulfur oxides cause various environmental pollution problems such as acid rain.

[0003] Desulfurization technology for removing sulfur oxides from industrial flue gas has been continuously studied, and a flue gas desulfurization method of treating flue gas after combustion of
20 fossil fuels has been generally used in factories or power plants.

[0004] The flue gas desulfurization method refers to a method of desulfurizing the flue gas after burning a fossil fuels containing sulfur, and the flue gas desulfurization methods are categorized into wet treatment and dry treatment. A wet treatment method removes sulfur oxides by washing flue gas with ammonia water, sodium hydroxide solution, lime milk, etc. while a dry treatment
25 method removes sulfur oxides by brining particles or powders of activated carbon or carbonates into contact with flue gas to adsorb or react with sulfur dioxide.

[0005] In particular, the sulfur oxide content of heavy fuel oil (MGO, MDO, DDO) such as bunker C oil used in marine engines is 1,000 to 3,000 times higher than that of automobile fuel. The amount of sulfur oxides emitted by ships around the world is 130 times higher than that by

automobiles and thus is known as the main cause of environmental pollution.

[0006] For this reason, conventionally, flue gas desulfurization, which is a post-treatment process performed after combustion of fuel, is used. The fuel gas desulfurization uses a marine wet desulfurization system to remove sulfur oxides emitted from marine engines. In the wet desulfurization system, a pump is used to supply washing water (NaOH), which is usually, to a scrubber through a cooler, and the washing water comes into contact with flue gas in the scrubber. In this case, sulfur oxides are removed through a post-treatment process.

[0007] In this case, to maintain or boost the sulfur oxide removal capability of the wet desulfurization system at or to a predetermined level, the pH of the washing water is monitored, and the supply amount of the washing water is automatically controlled. To recycle the washing water, the used washing water is purified, and a huge amount of sludge is generated during the purification of the washing water. The sludge is usually collected and stored in a sludge tank during sailing, and the sludge is treated after the ship is anchored.

[0008] The conventional wet desulfurization technique, which is a post-treatment process, requires a lot of manpower and operation cost due to the complicated washing water purification process, and it is necessary to construct an additional complex desulfurization facility. Therefore, it is difficult to apply such a conventional desulfurization system to currently operating ships. In other words, it is not easy or practical to use the conventional desulfurization system in an existing ship in terms of space and cost.

[0009] Therefore, in order to dramatically reduce the environmental pollution caused by the combustion of marine fuel oil and by the emission of sulfur oxides, research on an effective pretreatment desulfurization method that can significantly reduce the emission of sulfur oxides, can easily remove sulfur oxides, and can be easily applied to an existing ship is urgently needed.

Disclosure

Technical Problem

[0010] The present invention has been devised to solve the above problems, and the objective of the present invention is to provide a marine fuel oil pretreatment desulfurization method using a pretreatment desulfurization agent, the method being capable of preventing sulfur oxides generated

during combustion of high-sulfur marine fuel oil from being discharged into the atmosphere, being simple in procedure, being easily applicable, and exhibiting a good desulfurization effect.

Technical Solution

5 **[0011]** In order to solve the technical problem described above, in one aspect of the present invention, a pretreatment desulfurization agent is prepared. The pretreatment desulfurization agent includes: (a) at least one oxide selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO , Na_2O , K_2O , and P_2O_3 ; (b) at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb; and (c) at least one liquid composition selected from
10 the group consisting of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), and hydrogen peroxide (H_2O_2). The pretreatment desulfurization agent is introduced into a fuel supply line through which marine fuel oil is supplied to a marine engine at a certain ratio so that a fluid mixture containing the marine fuel oil and the pretreatment desulfurization agent is supplied to the marine engine, thereby adsorbing and removing sulfur
15 oxides during combustion of the fluid mixture.

[0012] In one embodiment, the oxide may include 15 to 90 parts by weight of SiO_2 , 15 to 100 parts by weight of Al_2O_3 , 10 to 50 parts by weight of Fe_2O_3 , 5 to 15 parts by weight of TiO_2 , 20 to 150 parts by weight of MgO , 10 to 20 parts by weight of MnO , 20 to 200 parts by weight of CaO , 15 to 45 parts by weight of Na_2O , 20 to 50 parts by weight of K_2O , and 5 to 20 parts by weight of
20 P_2O_3 . The metal may include 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd, and 0.003 to 0.005 parts by weight of Pb.

25 **[0013]** In addition, in one embodiment, the oxide and metal may have a particle size of 1 to 2 μm and a specific gravity of 2.5 to 3.0.

[0014] In addition, in one embodiment, the sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) may be contained in an amount of 20 to 130 parts by weight, the sodium hydroxide (NaOH) may be contained in an amount of 15 to 120 parts by weight, the sodium silicate (Na_2SiO_3) may be

contained in an amount of 50 to 250 parts by weight, and hydrogen peroxide (H₂O₂) may be contained in an amount of 10 to 50 parts by weight.

[0015] In addition, in one embodiment, in the pretreatment desulfurization agent, the oxide, the metal, and the liquid composition may form a metal chelate compound.

5 [0016] In addition, in one embodiment, the sulfur oxides (SO_x) adsorption effect of the pretreatment desulfurization agent may be activated at a temperature in a range of 400°C to 1200°C.

[0017] In addition, in one embodiment, the pretreatment desulfurization agent may be mixed in a ratio of 0.1 to 10 parts by weight with respect to 100 parts by weight of the marine fuel oil.

10 [0018] In addition, in one embodiment, the pretreatment desulfurization agent may be mixed in a ratio of 6 parts by weight with respect to 100 parts by weight of the marine fuel oil.

[0019] In addition, in one embodiment, the marine fuel oil and the pretreatment desulfurization agent may be mixed and supplied to the marine engine through line mixing.

[0020] In addition, in one embodiment, the marine fuel oil may be any one of heavy oil such as
15 bunker-A oil, bunker-B oil, or bunker-C oil, or light oil such as MGO, MDO, or DDO.

Advantageous Effects

[0021] According to the present invention, the marine fuel oil pretreatment desulfurization method using the pretreatment desulfurization agent can prevent a large amount of sulfur oxides
20 generated in a process of burning high-sulfur-content marine fuel oil from being emitted into the air in real time, thereby greatly contributing to solving the problem of air pollution caused by sulfur oxides.

[0022] In addition, the pretreatment desulfurization method of the present invention is different from a conventional desulfurization method in which exhaust gas is desulfurized after the
25 combustion of fuel. That is, the pretreatment desulfurization agent is mixed with marine fuel oil before the marine fuel oil is combusted, and the marine fuel oil and the pretreatment desulfurization agent are combusted together by a marine engine. The method of the present invention can be easily and simply applied to existing ships because an additional desulfurization facility is not required to use the method of the present invention. That is, only required is to

connect a pretreatment desulfurization agent supply line to an existing marine fuel oil supply line to use the method of the present invention. Therefore, the method of the present invention can be simply and easily applied to existing ships and can improve the desulfurization effect.

5 **Description of Drawings**

[0023] FIG. 1 is a view illustrating an exemplary construction of a pretreatment desulfurization system according to the present invention;

[0024] FIG. 2 is a partially enlarged view of a region A of FIG. 1;

10 [0025] FIG. 3 is a view illustrating the result of concentration analysis of sulfur oxide (SO₂) for the entire session of Experimental Example 1; and

[0026] FIG. 4 is a view illustrating the result of concentration analysis of sulfur oxide (SO₂) for the entire session of Experimental Example 2.

Best Mode

15 [0027] In the following description, the specific structural or functional descriptions for exemplary embodiments according to the concept of the present disclosure are merely for illustrative purposes, and those skilled in the art will appreciate that various modifications and changes to the exemplary embodiments are possible, without departing from the scope and spirit of the present disclosure. Therefore, the present disclosure is intended to cover not only the
20 exemplary embodiments but also various alternatives, modifications, equivalents, and other embodiments that may be included within the spirit and scope of the embodiments as defined by the appended claims. Hereinafter, embodiments of the present invention will be described in detail in conjunction with the accompanying drawings.

25 [0028] The present invention uses a desulfurization catalyst (hereinafter, referred to as “pretreatment desulfurization agent”) including: (a) at least one oxide selected from the group consisting of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MgO, MnO, CaO, Na₂O, K₂O, and P₂O₃; (b) at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb; and (c) at least one liquid composition selected from the group consisting of sodium tetraborate (Na₂B₄O₇·10H₂O), sodium hydroxide (NaOH), sodium silicate (Na₂SiO₃), and hydrogen peroxide

(H₂O₂).

[0029] The pretreatment desulfurization agent according to the present invention preferably includes at least one oxide selected from the group consisting of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MgO, MnO, CaO, Na₂O, K₂O, and P₂O₃. Preferably, the pretreatment desulfurization agent includes all of the oxides selected from the group consisting of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MgO, MnO, CaO, Na₂O, K₂O, and P₂O₃ as in one example described below.

[0030] When SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MgO, MnO, CaO, Na₂O, K₂O, and P₂O₃ are all included, the basic formula is K_{0.8-0.9}(Al,Fe,Mg)₂(Si,Al)₄O₁₀(OH)₂ which is a mineral commonly called illite. The illite has a 2:1 structure in which one octahedral layer is bonded between two tetrahedral layers. The octahedral layer has a dioctahedral structure in which only 2 cation sites out of 3 cation sites in the bonding structure are filled with cations. Due to the lack of a cation, the illite is overall negatively charged (-). For this reason, sulfur oxides (SO_x) can be adsorbed when the mixture of a combustible material and the desulfurization catalyst is burned.

[0031] As the oxides, the pretreatment desulfurization agent may include 15 to 90 parts by weight of SiO₂, 15 to 100 parts by weight of Al₂O₃, 10 to 50 parts by weight of Fe₂O₃, 5 to 15 parts by weight of TiO₂, 20 to 150 parts by weight of MgO, 10 to 20 parts by weight of MnO, and 20 to 200 parts by weight of CaO, 15 to 45 parts by weight of Na₂O, 20 to 50 parts by weight of K₂O, and 5 to 20 parts by weight of P₂O₃.

[0032] In addition, the oxides may be mixed and then pulverized into fine particles having a particle size of 1 to 2 μm by a pulverizer before being prepared as the desulfurization catalyst. The oxides may have a specific gravity of 2.5 to 3.0 and may be in the form of powder that is streak-colored or silvery white.

[0033] The pretreatment desulfurization agent according to the present invention may include one or more metals selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb. As in one embodiment, all of the metals including Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb are preferably included.

[0034] As the metals, the pretreatment desulfurization agent may include 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of

Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd, and 0.003 to 0.005 parts by weight of Pb.

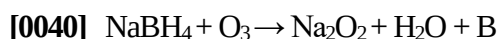
[0035] In addition, the metals, like the oxides, may be mixed and then pulverized into fine particles having a particle size of 1 to 2 μm by a pulverizer, the metals may have a specific gravity of 2.5 to 3.0, and the metals may be in the form of powder that is streak-colored and silvery white.

[0036] The pretreatment desulfurization agent according to the present invention may include at least one liquid composition selected from the group consisting of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), and hydrogen peroxide (H_2O_2). Preferably, as in one embodiment, all of the liquid compositions including sodium tetraborate, sodium hydroxide, sodium silicate, and hydrogen peroxide may be contained.

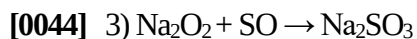
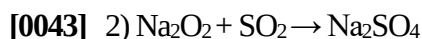
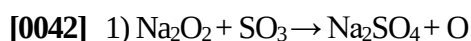
[0037] The pretreatment desulfurization agent according to the present invention forms a metal chelate compound through coordination with the metals because the oxides and the liquid compositions are mixed and reacted to serve as a chelating agent.

[0038] In addition, the liquid composition may be adsorbed on ash generated when a combustible material is combusted so that the liquid composition may react with sulfur oxides present in the ash, thereby removing the sulfur oxides. NaBO_2 is derived from the sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) undergoes hydrogenation to produce NaBH_4 , and the produced NaBH_4 reacts with oxygen and sulfur oxides to form sodium sulfate (Na_2SO_4). Thus, the sulfur oxides are removed. The reactions are represented by Reaction Formulas 1 and 2 below.

[0039] [Reaction Formula 1]



[0041] [Reaction Formula 2]



[0045] In addition, as the liquid compositions, the sodium tetraborate, the sodium hydroxide, the sodium silicate, and the hydrogen peroxide may be included in amounts of 20 to 130 parts by weight, 15 to 120 parts by weight, 50 to 250 parts by weight, and 10 to 50 parts by weight, respectively in the pretreatment desulfurization agent.

[0046] When the pretreatment desulfurization agent according to the present invention is mixed with a combustible material and combusted together at a temperature in a range of 400°C to 1200°C, the effect of adsorbing sulfur oxides can be activated. However, when the mixture is combusted in a temperature range of 600°C to 900°C, high efficiency can be obtained.

5 **[0047]** Hereinafter, a method of preparing the pretreatment desulfurization agent according to the present invention will be described.

[0048] The pretreatment desulfurization agent according to the present invention is prepared through a method including: (a) preparing an oxide powder by mixing and finely pulverizing at least one oxide selected from the group consisting of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MgO, MnO, CaO,
10 Na₂O, K₂O, and P₂O₃; (b) preparing a metal powder by mixing and finely pulverizing at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb; and (c) mixing the oxide mixture prepared in (a) and the metal mixture prepared in (b) with at least one liquid composition selected from the group consisting of sodium tetraborate (Na₂B₄O₇·10H₂O), sodium hydroxide (NaOH), sodium silicate (Na₂SiO₃), and hydrogen peroxide (H₂O₂).

15 **[0049]** In step (a), the oxide powder including at least one oxide selected from the group consisting of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MgO, MnO, CaO, Na₂O, K₂O, and P₂O₃ is mixed and finely ground with a fine pulverizer.

[0050] In this step, the oxide powder includes 15 to 90 parts by weight of SiO₂, 15 to 100 parts by weight of Al₂O₃, 10 to 50 parts by weight of Fe₂O₃, 5 to 15 parts by weight of TiO₂, 20 to 150 parts
20 by weight of MgO, 10 to 20 parts by weight of MnO, and 20 to 200 parts by weight of CaO, 15 to 45 parts by weight of Na₂O, 20 to 50 parts by weight of K₂O, and 5 to 20 parts by weight of P₂O₃.

[0051] In addition, the finely ground oxide powder may be ground repeatedly until the particle size of the powder falls within a range of 1 to 2 μm.

[0052] In step (b), the metal powder including at least one metal selected from the group
25 consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd and Pb is mixed and ground with a fine pulverizer.

[0053] The metal powder may include 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd, and 0.003 to 0.005

parts by weight of Pb.

[0054] In addition, the finely ground metal powder may be ground repeatedly until the particle size of the powder falls within a range of 1 to 2 μm .

5 **[0055]** In step (c), at least one liquid composition selected from the group consisting of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), and hydrogen peroxide (H_2O_2) is mixed with the finely ground oxide powder and the finely ground metal powder prepared in step (a) and step (b) to prepare a desulfurization catalyst.

10 **[0056]** In this step, the sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) may be contained in an amount of 20 to 130 parts by weight, the sodium hydroxide (NaOH) may be contained in an amount of 15 to 120 parts by weight, the sodium silicate (Na_2SiO_3) may be contained in an amount of 50 to 250 parts by weight, and the hydrogen peroxide (H_2O_2) may be contained in an amount of 10 to 50 parts by weight.

15 **[0057]** In addition, in this step, when mixing and reacting the mixed and finely ground oxide and metal powders prepared in steps (a) and (b), the oxide powder and the liquid composition act as a chelating agent so that a metal chelate compound can be formed.

[0058] In addition, the pretreatment desulfurization agent formed in this step is stabilized by sedimentation for 24 to 72 hours, and the sedimented pretreatment desulfurization agent is separated and dried naturally to be used as a powder catalyst for desulfurization. The liquid composition remaining after the sedimented desulfurization catalyst is separated may be used as a
20 liquid catalyst for desulfurization.

[0059] In addition, in the desulfurization method using the pretreatment desulfurization agent according to the present invention, the desulfurization function may be activated when it is mixed and combusted with a combustible material.

25 **[0060]** A conventional desulfurization method removes sulfur oxides (SO_x) from flue gas generated during combustion of a combustible material. The conventional method requires a desulfurization facility for performing the desulfurization process and incurs manpower and cost for operating the desulfurization facility. However, since the desulfurization method of the present invention burns the pretreatment desulfurization agent along with the combustible material, the pretreatment desulfurization agent removes sulfur oxides through adsorption during the

combustion, thereby reducing the content of sulfur oxides in flue gas. In this way, the method of the present invention exhibits a desulfurization effect.

[0061] In addition, the combustible material to which the pretreatment desulfurization agent according to the present invention can be applied may be a combustible material that generates heat through combustion. Examples of the combustible material include coal, petroleum, waste, and biogas.

[0062] In addition, as described above, the pretreatment desulfurization agent is separated into a powder catalyst for desulfurization and a liquid catalyst for desulfurization. Each of the powder catalyst and the liquid catalyst is used alone or in combination with the other, depending on the contents of C, H, N, and S of the combustible material. Therefore, the pretreatment desulfurization agent of the present invention can exhibit an excellent desulfurization effect in a simple and easy way of use.

[0063] Hereinafter, the configuration of a pretreatment desulfurization system according to one embodiment of the present invention, which is to be applied to a marine engine, will be described in detail with reference to FIG. 1.

[0064] The pretreatment desulfurization system according to the present invention is connected to a fuel supply line 30 of a marine engine 70 to supply the pretreatment desulfurization agent (liquid catalyst for desulfurization) in a certain mixing ratio with respect to fuel.

[0065] Usually, as the fuel of the marine engine 70, marine fuel oil, for example, heavy oil such as bunker-A oil, bunker-B oil, or bunker-C oil, or light oil such as MGO, MDO, or DDO is used. Among them, bunker C oil is a high sulfur oil and generates a large amount of sulfur oxides during combustion thereof. Therefore, the use of bunker-C oil is regulated due to air pollution.

[0066] In FIG. 1, reference numerals 10, 20, 30, 40, 50, and 60 denote a fuel tank, a fuel supply pump, a fuel supply line, a fuel filter, an injection pump, and an injection nozzle, respectively. A detailed description of the components will be omitted.

[0067] To this end, the pretreatment desulfurization system according to the present invention is equipped with a desulfurization agent tank 110 having a predetermined volume for storing the pretreatment desulfurization agent, and one end of the desulfurization agent tank 110 is connected to a metering pump 130 for quantitatively supplying the pretreatment desulfurization agent.

[0068] In addition, a flow meter 120 for checking the input flow rate of the pretreatment desulfurization agent, a check valve 140 for adjusting the input flow rate, and a pressure gauge 150 are installed on the fuel supply line 30 between the metering pump 130 and the marine engine 70. Therefore, it is possible to continuously check the fuel supply amount to the marine engine 70 and regulate the supply of the pretreatment desulfurization agent so that the pretreatment desulfurization agent is supplied in a predetermined ratio with respect to the fuel supply amount.

[0069] The pretreatment desulfurization agent is preferably supplied and mixed in an amount of 0.1% to 10% by weight relative to 100% by weight of the marine fuel oil.

[0070] Referring to FIG. 2, the pretreatment desulfurization agent is connected to a line mixer 160 provided on the fuel supply line 30 for supplying the marine fuel oil, and the pretreatment desulfurization agent injected from one side and the marine fuel oil are sufficiently mixed in the line mixer 160 (this process is called line mixing). The sufficiently mixed fluid mixture of the marine fuel oil and the pretreatment desulfurization agent is supplied to the marine engine.

[0071] Thereafter, the fluid mixture is combusted in the marine engine. Therefore, sulfur oxides generated during a combustion process are adsorbed and removed by the pretreatment desulfurization agent before being discharged to the outside.

[0072] Through this process, even when high-sulfur marine fuel oil such as bunker-C oil is used as fuel, since sulfur oxides are almost perfectly removed during the combustion, it is possible to solve the air pollution problem caused by sulfur oxides.

[0073] Hereinafter, the present invention will be described in more detail with reference to Examples and Test Examples.

[0074] Examples and Test Examples presented herein are only for illustrative purposes and are not intended to limit the scope of the present invention.

[0075] <Example> Preparation of Pretreatment Desulfurization Agent

[0076] As oxides, SiO₂ 150 kg, Al₂O₃ 150 kg, Fe₂O₃ 100 kg, TiO₂ 50 kg, MgO 200 kg, MnO 100 kg, CaO 200 kg, Na₂O 150 kg, K₂O 200 kg, and P₂O₃ 50 kg were mixed and finely ground to form fine oxide powder.

[0077] As metals, Li 35 g, Cr 50 g, Co 10 g, Ni 60 g, Cu 180 g, Zn 350 g, Ga 400 g, Sr 200 g, Cd 20 g, and Pb 30 g were mixed and finely ground to form fine metal powder.

[0078] The fine oxide powder and the fine metal powder are repeatedly ground to have a particle size of 1 to 2 μm .

[0079] 3000 kg of water was put into a reactor, the water was maintained at a temperature of 50°C to 60°C, and 50 kg of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) were added thereto. After stirring for 30 minutes, 100 kg of sodium hydroxide (NaOH) was added and stirred. Next, after 10 minutes, the fine oxide powder was added in units of 100 kg at intervals of 5 minutes and stirred for 2 hours or more. While stirring, the temperature was raised to 60°C to 80°C, and 100 kg of sodium silicate (Na_2SiO_3) was added. After stirring for 30 minutes, the fine metal powder was added in units of 20 g at intervals of 3 minutes and stirred. After stirring for 1 hour, 30 kg of hydrogen peroxide (H_2O_2) was added, stirred for another 30 minutes, and then naturally cooled for 1 hour.

[0080] After cooling and stabilizing for 48 hours, the liquid composition and the sedimented powder composition are separated from each other.

[0081] The sedimented powder composition was dried naturally and named as a powder catalyst for desulfurization (GTS-P).

[0082] In addition, the liquid composition remaining after the sedimented powder composition was removed was moved to a separate container and named as a liquid catalyst for desulfurization (GTS-W).

[0083] <Experimental Example 1> Test For Checking Reduction in Sulfur oxide in Marine Engine Exhaust Gas

[0084] (1) Test Condition

[0085] In order to evaluate the desulfurization efficiency of the pretreatment desulfurization agent (liquid catalyst for desulfurization) prepared as described above, 3.5% and 6.0% by weight of the pretreatment desulfurization agent was supplied to a fuel supply line connected to a marine engine so as to be mixed with 100% by weight of fuel, and the mixture was burned. Next, a sulfur oxide reduction performance test was conducted to analyze and compare the concentration of sulfur oxides in exhaust gas.

[0086] The specifications of the marine engine used for the test are shown in Table 1 below.

[0087] [Table 1] Specifications of engine for test

Maker	Yanmar
Model	4LOD
Horse power (Hp)	200
Number of Cylinders	4 in-line
Combustion system	Direct injection
Aspiration	Natural aspirated
Dimensions (L x W x H, mm)	500 X 1550 X 1400
Cooling system	Direct water cooling
Marine gear	Mechanical
Fuel consumption rate	100mL/min

[0088] ○ Fuel used: bunker-C oil

[0089] ○ Operation condition: no-load operation

[0090] ○ Supply amount and method of pretreatment desulfurization agent: 3.5% and 6.0% by weight of the pretreatment desulfurization agent was mixed and supplied to the fuel supply line with a metering pump with respect to the fuel flow rate.

[0091] ○ Marine engine exhaust gas analysis system: German VarioPlus Ind. MRU Emission Monitoring System

[0092] ○ Marine engine exhaust gas analysis method: exhaust gas was sampled from an exhaust pipe connected to an engine and was analyzed with an analysis system (standard oxygen concentration of 17%)

[0093] * Since the oxygen concentration in the exhaust gas was maintained at 17% to 18% in the engine no-load operation condition, the reference oxygen concentration was set to 17% to prevent an excessive difference between the measured concentration and the corrected concentration that is based on the reference oxygen concentration.

[0094] (2) Test Method and Procedures

[0095] 1) Main engine operation state and normal state

[0096] 2) Preheat exhaust gas analysis system and perform zero setting

[0097] 3) Perform measurement in a condition in which no pretreatment desulfurization agent was injected (30 minutes)

[0098] 4) Perform measurement in a condition in which 6.0% by weight of pretreatment

desulfurization agent was injected (1 hour)

[0099] 5) Repeat step 3) and step 4) one more time

[0100] 6) Perform measurement in a condition in which no pretreatment desulfurization agent was injected (30 minutes)

5 **[0101]** 7) Perform measurement in a condition in which 3.5% by weight of pretreatment desulfurization agent was injected (1 hour)

[0102] 8) Perform measurement in a condition in which no pretreatment desulfurization agent was injected (30 minutes)

[0103] 9) Perform measurement in a condition in which 6.0% by weight of pretreatment desulfurization agent was injected (1 hour)

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[0104] 10) Save data and stop analysis

[0105] [Table 2] Test Condition

Time	Test condition
11:21-11:54	Fuel oil
11:54-13:20	Pretreatment desulfurization agent 6.0% by weight
13:20-14:03	Fuel oil
14:03-15:06	Pretreatment desulfurization agent 6.0% by weight
15:06-15:46	Fuel oil
15:46-16:46	Pretreatment desulfurization agent 3.5% by weight
16:46-17:23	Fuel oil
17:23-18:25	Pretreatment desulfurization agent 6.0% by weight

[0106] (3) Result of Analysis of Sulfur Oxide (SO₂) Concentration (in Terms of 17% Reference Oxygen Concentration)

15 **[0107]** FIG. 3 shows the analysis results of sulfur oxide (SO₂) concentration for the entire session of Experimental Example 1 performed according to the test conditions, methods, and procedures described above, and Table 3 summarizes data of the values of SO₂ concentration in each measurement session of FIG. 3. (in terms of 17% of reference oxygen concentration)

[0108] [Table 3] SO₂ concentration for measurement session (in terms of 17% of reference oxygen concentration)

Measurement time	Test condition	SO ₂ concentration (ppm)	Note
11:35-12:00	Fuel oil	102.00	Average value
12:23-13:00	Pretreatment desulfurization agent 6.0% by weight	0.01	Average value
14:08	Fuel oil	100.0	Peak value
14:26-15:15	Pretreatment desulfurization agent 6.0% by weight	0.00	Average value
15:51	Fuel oil	95.2	Peak value
16:22-16:52	Pretreatment desulfurization agent 3.5% by weight	29.19	Average value
17:28	Fuel oil	94.5	Peak value
17:50-18:25	Pretreatment desulfurization agent 6.0% by weight	0.00	Average value

[0109] Referring to FIG. 3 and Table 3, after 6.0% by weight and 3.5% by weight of the pretreatment desulfurization agent relative to 100% by weight of the fuel oil were sequentially injected into the fuel supply line, the concentration of SO₂ was measured for each case. That is, the test was performed with four measurement sessions.

[0110] In a first measurement session, when only fuel oil was burned (measurement time: 11:35-12:00), the concentration of SO₂ in the exhaust gas was 102.00 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was added (measurement time: 12:23-13:00), the concentration of SO₂ rapidly dropped to 0.01 ppm.

[0111] In a second measurement session, when only fuel oil was burned (measurement time: 14:08), the concentration of SO₂ in the exhaust gas was 100.00 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was added relative to 100% by weight of fuel oil (measurement time: 14:26-15:15), the concentration of SO₂ rapidly dropped to 0.00 ppm.

[0112] In a third measurement session, when only fuel oil was burned (measurement time 15:51), the concentration of SO₂ in the exhaust gas was 95.2 ppm, but when 3.5% by weight of the pretreatment desulfurization agent was added relative to 100% by weight of fuel oil (measurement time 16:22-16:52), the concentration of SO₂ rapidly dropped to 29.19 ppm.

[0113] In a fourth measurement session, when only fuel oil was burned (measurement time: 17:28), the concentration of SO₂ in the exhaust gas was 94.5 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was added relative to 100% by weight of fuel oil (measurement time: 17:50-18:25), the concentration of SO₂ rapidly dropped to 0.00 ppm.

5 **[0114]** The measurement results showed that the effect of reducing the SO₂ emissions was improved when the mixing ratio of the pretreatment desulfurization agent was increased from 3.5% by weight to 6.0% by weight.

[0115] <Experimental Example 2> Test For Checking Reduction in Sulfur oxide in Marine Engine Exhaust Gas

10 **[0116]** (1) Test Condition

[0117] The same as in Test Example 1

[0118] (2) Test Method and Procedures

[0119] The same as in Test Example 1

[0120] [Table 4] Test Condition

Time	Test condition
09:06-09:44	Fuel oil
09:44-10:54	Pretreatment desulfurization agent 3.5% by weight
10:54-11:10	Fuel oil
11:10-11:37	Engine stop
11:37-13:02	Fuel oil
12:02-13:08	Pretreatment desulfurization agent 6.0% by weight

15 **[0121]** (3) Result of Analysis of Sulfur Oxide (SO₂) Concentration (in Terms of 17% Reference Oxygen Concentration)

[0122] FIG. 4 shows the analysis results of sulfur oxide (SO₂) concentration for the entire session of Experimental Example 2 performed according to the test conditions, methods, and procedures described above, and Table 5 summarizes data of the values of SO₂ concentration in each measurement session of FIG. 4. (In terms of a reference oxygen concentration of 17%)

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[0123] [Table 5] SO₂ concentration for each measurement session (in terms of the reference oxygen concentration of 17%)

Measurement time	Test condition	Concentration of SO ₂ (ppm)	Note
09:12-09:40	Fuel oil	96.43	Average value
10:18-10:51	Pretreatment desulfurization agent 3.5% by weight	29.54	Average value
11:55-12:44	Fuel oil	98.93	Average value
12:57-13:06	Pretreatment desulfurization agent 6.0% by weight	0.00	Average value

[0124] Referring to FIG. 4 and Table 5, after 6.0% by weight and 3.5% by weight of the pretreatment desulfurization agent relative to 100% by weight of the fuel oil were injected into the fuel supply line, the concentration of SO₂ was measured for each case. That is, the test was performed with two measurement sessions.

[0125] In a first measurement session, when only fuel oil was burned (measurement time: 09:12-09:40), the concentration of SO₂ in the exhaust gas was 96.43 ppm, but when 3.5% by weight of the pretreatment desulfurization agent was input relative to 100% by weight of fuel oil (measurement time: 10:18-10:51), the concentration of SO₂ rapidly dropped to 29.54 ppm.

[0126] In a second measurement session, when only fuel oil was burned (measurement time: 11:55-12:44), the concentration of SO₂ in the exhaust gas was 98.93 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was input relative to 100% by weight of fuel oil (measurement time: 12:57-13:06), the concentration of SO₂ rapidly dropped to 0.00 ppm.

[0127] The measurement results showed that the effect of reducing the SO₂ emissions was improved when the mixing ratio of the pretreatment desulfurization agent was increased from 3.5% by weight to 6.0% by weight.

[0128] As can be seen from the results of Experimental Examples 1 and 2, when fuel and the pretreatment desulfurization agent were burned together, the SO₂ concentration in the exhaust gas was reduced by at least 69% and by 100% at a maximum compared to the case where only fuel is burned. In addition, when the pretreatment desulfurization agent was increased from 3.5% by

weight to 6.0% by weight, the reduction in the SO₂ emissions was increased.

Industrial Applicability

[0129] The present invention can be widely used for pretreatment desulfurization for marine fuel oil.

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CLAIMS

1. A marine fuel oil pretreatment desulfurization method using a pretreatment desulfurization agent, the method comprising:

5 preparing a pretreatment desulfurization agent comprising (a) at least one oxide selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO , Na_2O , K_2O , and P_2O_3 , (b) at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb, and (c) at least one liquid composition selected from the group consisting of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3) and hydrogen peroxide
10 (H_2O_2);

feeding the pretreatment desulfurization agent, at a predetermined ratio, to a marine engine fuel supply line that transports marine fuel oil to a marine engine so that a fluid mixture containing the marine fuel oil and the pretreatment desulfurization agent is supplied to the marine engine, thereby adsorbing and removing sulfur oxides during combustion of the fluid mixture.

15 2. The method according to claim 1, wherein the oxide comprises 15 to 90 parts by weight of SiO_2 , 15 to 100 parts by weight of Al_2O_3 , 10 to 50 parts by weight of Fe_2O_3 , 5 to 15 parts by weight of TiO_2 , 20 to 150 parts by weight of MgO , 10 to 20 parts by weight of MnO , 20 to 200 parts by weight of CaO , 15 to 45 parts by weight of Na_2O , 20 to 50 parts by weight of K_2O , and 5
20 to 20 parts by weight of P_2O_3 , and the metal comprises 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd, and 0.003 to 0.005 parts by weight of Pb.

25 3. The method according to claim 1, wherein the oxide and metal have a particle size of 1 to 2 μm and a specific gravity of 2.5 to 3.0.

4. The method according to claim 1, wherein the sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is

contained in an amount of 20 to 130 parts by weight, the sodium hydroxide (NaOH) is contained in an amount of 15 to 120 parts by weight, the sodium silicate (Na₂SiO₃) is contained in an amount of 50 to 250 parts by weight, and the hydrogen peroxide (H₂O₂) is contained in an amount of 10 to 50 parts by weight.

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5. The method according to claim 1, wherein the pretreatment desulfurization agent is configured such that the oxide, the metal, and the liquid composition form a metal chelate compound.

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6. The method according to claim 1, wherein the pretreatment desulfurization agent has a sulfur oxide (SO_x) adsorption effect that is activated at temperatures in a range of 400°C to 1200°C.

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7. The method according to claim 1, wherein the pretreatment desulfurization agent is mixed in a ratio of 0.1 to 10 parts by weight with respect to 100 parts by weight of the marine fuel oil.

8. The method according to claim 1, wherein the pretreatment desulfurization agent is mixed in a ratio of 6 parts by weight with respect to 100 parts by weight of the marine fuel oil.

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9. The method according to claim 1, the marine fuel oil and the pretreatment desulfurization agent are mixed and supplied to the marine engine through line mixing.

10. The method according to claim 1, wherein the marine fuel oil is heavy oil such as bunker-A oil, bunker-B oil, or bunker-C oil, or light oil such as MGO, MDO, or DDO.